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REACTIONS OF SULFUR ATOMS

by

EDWARD LEWIS DEDIO

A THESIS

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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies for acceptance, a
thesis entitled:

"REACTIONS OF SULFUR ATOMS,"

submitted by Edward Lewis Dedio in partial fulfilment of the
requirements for the degree of Doctor of Philosophy.



ABSTRACT

The reaction of sulfur atoms have been examined with cyclopentene, cyclohexene and perfluorocyclobutene. Addition of sulfur atoms to the double bond and statistical insertion of $S(^1D)$ atoms into alkenylic C-H bonds was observed for the hydrocarbons, resulting in formation of the corresponding episulfides and mercaptans respectively. Vinylic mercaptans are formed in only small quantities. Perfluorination results in a decreased reactivity, however, a short-lived cyclo- C_4F_6 episulfide was formed in the reaction of sulfur atoms with perfluorocyclobutene.

Insertion of $S(^1D)$ atoms into the methyl groups of trimethylethylene and tetramethylethylene have been observed. Comparison of the data with that available for other methylated ethylenes suggests that the reactivity of $S(^1D)$ atoms towards the π -bond is unaffected by the amount of alkyl substitution on the double bond.

Sulfur atoms react with vinyl chloride to yield episulfide (ca. 85%) and 2-chlorovinyl mercaptan (ca. 15%). Considerable polymerisation also occurs. Vinyl chloride is 1.4 times more reactive than ethylene towards $S(^3P)$ atom addition, resulting from a lower activation energy for the addition process in the case of vinyl chloride.

The reaction of $S(^1D)$ atoms with cis and trans-1,2-dichloroethenes results in a sulfur atom initiated polymerisation of the olefin. Reaction of $S(^3P)$ atoms results in episulfide formation resulting from stereospecific addition of $S(^3P)$ atoms to the double bond.

$S(^1D)$ atoms insert into C-H bonds of alkyl chlorides resulting in formation of hot chloro mercaptans, which decompose by HCl elimination. No insertion into C-Cl bonds was observed.

Possible transition complexes for sulfur atom reactions are discussed. Insertion into alkenylic C-H bonds appears to occur by direct insertion via a three-centered transition complex while vinylic mercaptans probably arise from rearrangement of hot singlet biradicals. Electrophilic addition of $S(^3P)$ atoms to olefins suggests formation of a charge-transfer complex in the transition state, but, steric hindrance suggests that reactivity is probably with a particular carbon center rather than with the double bond as a whole.

The reactions of sulfur atoms with a series of acetylenes have been observed. From these studies it was concluded that the major reaction is a sulfur atom initiated polymerisation of the alkyne. Small yields of the thiophenes and benzenes were also observed. Flash photolysis-kinetic mass spectrometry techniques indicate the presence of initial sulfur atom acetylene adducts. It was concluded that unstable thiacyclopropenes and/or thioketenes are reaction intermediates in these systems.

Reaction of sulfur atoms with perfluorobutyne-2 yielded mainly perfluorotetramethyl thiophene (ca. 50% of the sulfur atoms consumed). No insertion products were observed with the acetylenes.

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TABLE OF CONTENTS

<u>TITLE</u>	<u>Page</u>
ABSTRACT	i
ACKNOWLEDGMENTS	iv
LIST OF TABLES	ix
LIST OF ILLUSTRATIONS	xii
CHAPTER I	
INTRODUCTION	1
Methylene Chemistry	
Carbon Atoms	
Oxygen Atoms	
Se Atoms	
NH Radicals	
Sulfur Atoms	
Objectives and Scope of the Present Investigation	
CHAPTER II	
EXPERIMENTAL	34
STATIC SYSTEM	
1) The High-vacuum Apparatus	
2) Photolytic Assembly	
3) Analytical Assembly	
4) Experimental Procedures	
FLASH PHOTOLYSIS-KINETIC MASS SPECTROMETRY	
1) Apparatus	
2) Procedure	
FLASH PHOTOLYSIS	

<u>TITLE</u>	<u>Page</u>
CHAPTER III	
THE REACTION OF SULFUR ATOMS WITH:	52
1) Cyclopentene	
Results	
2) Cyclohexene	
Results	
3) Perfluorocyclobutene	
Results	
4) Trimethylethylene	
Results	
5) Tetramethylethylene	
Results	
DISCUSSION	
CHAPTER IV	
REACTIONS OF SULFUR ATOMS WITH CHLORINE	
CONTAINING COMPOUNDS	92
A) Reactions of Sulfur Atoms with Vinyl	
Chloride	
i. Results	
ii. Discussion	
B) Reactions of Sulfur Atoms with <u>Cis</u>	
and <u>Trans</u> -1,2-dichloroethenes	
i. Results	
ii. Discussion	
C) Reactions of Sulfur Atoms with Chloro	
Alkanes	

<u>TITLE</u>	<u>Page</u>
CHAPTER IV - continued	
i. Results	
ii. Discussion	
CHAPTER V	
TRANSITION COMPLEXES INVOLVED IN THE	
REACTIONS OF SULFUR ATOMS WITH OLEFINS	140
A) Reaction with Alkenylic C-H Bonds	
B) Reaction with Vinylic C-H Bonds	
C) Reactivity of Sulfur Atoms with the	
Double Bond	
CHAPTER VI	
REACTIONS OF SULFUR ATOMS WITH ACETYLENE	
AND SUBSTITUTED ACETYLENES	158
1) Reactions of Sulfur Atoms with Acetylene	
Results	
2) Reactions of Sulfur Atoms with Methyl	
Acetylene	
Results	
3) Reactions of Sulfur Atoms with	
Dimethyl Acetylene	
Results	
4) Reactions of Sulfur Atoms with	
Perfluorobutyne-2	
Results	
5) Reactions of Sulfur Atoms with a Mixture	
of Acetylene and Perfluorobutyne-2	
Results	
DISCUSSION	

<u>TITLE</u>	<u>Page</u>
CHAPTER VII SUMMARY AND CONCLUSIONS	208
APPENDIX A MASS SPECTRAL DATA	213
BIBLIOGRAPHY	221
VITA	229

LIST OF TABLES

<u>TABLE</u>		<u>Page</u>
I	Relative Rates of Addition of S(³ P), O(³ P) and Se(³ P) Atoms to Olefins	20
II	G.L.C. Operating Conditions and Elution Times for Sulfur Compounds	42
III	Materials Used	45
IV	Variation in Products Yields with Cyclo- pentene Pressure in the COS-Cyclopentene System	59
V	Variation in Product Yields as a Function of Added CO ₂ in the COS-Cyclopentene System	61
VI	Variation in Product Yields with Time in the COS-Cyclopentene System (Mercury Lamp).	63
VII	Variation in Product Yields with Reaction Time in the COS-Cyclopentene System (Cadmium Lamp).	66
VIII	Variation in Product Yields with Per- fluorocyclobutene Pressure in the COS-C ₄ F ₆ System	70
IX	Variation in Product Yields as a Function of Added Perfluorocyclobutene in the COS-Cyclopentene System	73
X	Percentage Insertion into Methyl C-H Bonds for a Series of Methylated Ethylenes	88

TABLEPage

XI	Variation in Product Yields with Vinyl Chloride Pressure in the COS- Vinyl Chloride System	94
XII	Variation in Product Yields as a Function of Added CO ₂ in the COS-Vinyl Chloride System	96
XIII	Product Yields in the COS-Vinyl Chloride- Propylene System	99
XIV	Relative Rates of Addition of S(³ P) Atoms to Olefins	106
XV	Variation in Product Distribution as a Function of Methyl Chloride Pressure in the COS-Methyl Chloride System	122
XVI	Variation in Product Yields as a Function of CF ₂ HCl Pressure in the COS-CF ₂ HCl System . . .	126
XVII	Variation in Product Yields as a Function of Ethyl Chloride Pressure in the COS- C ₂ H ₅ Cl System	129
XVIII	Relative Reactivity of Radical Reagents with a Series of Olefins	147
XIX	Relative Reactivity of Electrophilic Reagents with a Series of Olefins	151
XX	Variation in Product Yields with Acetylene Pressure in the COS-Acetylene System	160

<u>TABLE</u>		<u>Page</u>
XXI	CO Formation as a Function of Substrate Pressure in the COS-Methyl Acetylene System	173
XXII	Variation in Product Yields with Perfluorobutyne-2 Pressure in the COS-C ₄ F ₆ System	184
XXIII	Variation in Product Yields with CO ₂ Pressure in the COS-CO ₂ -Perfluorobutyne-2 System	187

LIST OF ILLUSTRATIONS

<u>Number</u>		<u>Page</u>
1)	High Vacuum Apparatus	35
2)	Photolysis Apparatus	37
3)	Analytical Apparatus	39
4)	Flash Photolysis-Kinetic Mass Spectrometry Apparatus	49
5)	Nuclear Magnetic Resonance Spectrum of a Mixture of Cyclopentene-3-thiol and Cyclopentene-4-thiol	55
6)	Nuclear Magnetic Resonance Spectrum of Cyclopentene Episulfide	57
7)	Variation in Product Yields with Cyclopentene Pressure in the COS-Cyclopentene System	60
8)	Variation in Product Yields as a Function of Added CO ₂ in the COS-Cyclopentene System	62
9)	Variation in Product Yields with Time in the COS-Cyclopentene System	64
10)	Nuclear Magnetic Resonance Spectrum of a Mixture of Cyclohexene-3-thiol and Cyclohexene-4-thiol	68
11)	CO Formation as a Function of Perfluorocyclobutene Pressure in the COS-Perfluorocyclobutene System .	71

<u>Number</u>		<u>Page</u>
12)	Variation in Product Yields as a Function of Added Perfluorocyclobutene in the COS-Cyclopentene System	74
13)	Oscillogram; Mass 194, $\text{C}_4\text{F}_6\text{S}$	75
14)	Oscillogram; Mass 194, $\text{C}_4\text{F}_6\text{S}$, Corrected for Bleed-out	75
15)	$\text{R}^{\text{O}}(\text{CO})/2$ / $\text{R}(\text{CO})-\text{R}^{\text{O}}(\text{CO})/2$ vs. Olefin/COS for the COS-Cyclopentene System	85
16)	Variation in Product Yields with Vinyl Chloride Pressure in the COS-Vinyl Chloride System	95
17)	Product Formation as a Function of Added CO_2 in the COS-Vinyl Chloride System	97
18)	Variation in Episulfide Yield as a Function of CO Yield in the COS-Vinyl Chloride- Propylene System	100
19)	Ionisation Potential vs. Log k for $\text{S}(^3\text{P})$ Atom Addition to Olefins	107
20)	Oscillogram; Mass 128, $\text{C}_2\text{H}_2\text{Cl}_2\text{S}$, First Signal	110
21)	Oscillogram; Mass 128, $\text{C}_2\text{H}_2\text{Cl}_2\text{S}$, After Several Flashes	110
22)	Oscillogram; Mass 128, $\text{C}_2\text{H}_2\text{Cl}_2\text{S}$, First Signal	111

<u>Number</u>		<u>Page</u>
23)	Oscillogram; Mass 128, $C_2H_2Cl_2S$, After Several Flashes	111
24)	Oscillogram; Mass 128, $C_2H_2Cl_2S$, Corrected for Bleed-out.	112
25)	Oscillogram; Normal Signal for Stable Volatile Product After Bleed-out Correction	112
25a)	Components of the $C_2H_2Cl_2S$ Signal	114
26)	CO Production as a Function of Methyl Chloride Pressure in the COS- Methyl Chloride System	123
27)	Oscillogram; Mass 82, CH_3ClS	124
28)	CO Formation as a Function of Chlorodifluoromethane Pressure in the COS-Chlorodifluoromethane System	127
29)	$R(CO)-R^O(CO)/2$ and CO Formation as a Function of Ethyl Chloride Pressure in the COS- Ethyl Chloride System	130
30)	Nuclear Magnetic Resonance Spectrum of 2-chloro-2-methyl-propane-1-thiol	132
31)	Potential Energy-Reaction Coordinate Diagram for Reaction of Radicals with Olefins	149
32)	Potential Energy-Reaction Coordinate Diagram for Reactions of Electrophilic Radicals with Olefins	152

<u>Number</u>		<u>Page</u>
33)	Potential Energy-Reaction Coordinate Diagram for Reaction of Sulfur Atoms with Olefins	155
34)	CO Formation as a Function of Acetylene Pressure in the COS-Acetylene System	161
35)	Product Formation as a Function of Acetylene Pressure in the COS-Acetylene System	163
36)	Oscillogram; Mass 58, C_2H_2S	164
37)	Oscillogram; Mass 58, C_2H_2S , Corrected for Bleed-out	164
38)	Oscillogram; Mass 58, C_2H_2S	165
39)	Oscillogram; Mass 76, Carbon Disulfide	165
40)	Oscillogram; Mass 78, Benzene	166
41)	Oscillogram; Mass 84, Thiopene	166
42)	Absorption Spectrum of Flashed Mixture of COS and Acetylene	169
43)	CO Formation as a Function of Methyl Acetylene Pressure in the COS-Methyl Acetylene System	174
44)	Oscillogram; Mass 72, C_3H_4S	175
45)	Oscillogram; Mass 72, C_3H_4S ., Signal Corrected for Bleed-out.	175
46)	Oscillogram; Mass 112, Dimethyl Thiopene	176
47)	Oscillogram; Mass 120, Trimethyl Benzene	176
48)	Oscillogram; Mass 86, C_4H_6S	178
49)	Oscillogram; Mass 86, C_4H_6S , Corrected for Bleed-out	178

<u>Number</u>		<u>Page</u>
50)	Oscillogram; Mass 140, Tetramethyl Thiophene	179
51)	Oscillogram; Mass 140, Tetramethyl Thiophene	179
52)	Oscillogram; Mass 86, C_4H_6S	181
53)	Oscillogram; Mass 86, C_4H_6S , Corrected for Bleed-out	181
54)	Absorption Spectrum of Flashed Mixture of COS and Dimethyl Acetylene	182
55)	CO Formation as a Function of Perfluorobutyne- 2 Pressure in the COS-Perfluorobutyne-2 System	185
56)	Product Variation as a Function of Perfluorobutyne-2 Pressure in the COS- Perfluorobutyne-2 System	186
57)	Product Variation as a Function of Added CO_2 in the COS-Perfluorobutyne-2 System	188
58)	Oscillogram; Mass 194, C_4F_6S	189
59)	Oscillogram; Mass 194, C_4F_6S	189
60)	Oscillogram; Mass 194, C_4F_6S Corrected for Bleed-out	190
61)	Nuclear Magnetic Resonance Spectrum of 2,3-perfluorodimethyl thiophene	192

CHAPTER I

INTRODUCTION

"Free radicals are complexes of abnormal valency which possess additive properties, but do not carry an electrical charge and are not free ions." This early definition of a free radical, by Wieland in 1915 (1), was one of the first attempts to define the components that make up a molecule; components which were recognized, although not identified, as early as the beginning of the nineteenth century.

The great interest in free radicals, shown in the early part of the twentieth century, was largely due to Gomberg's discovery of trivalent carbon in the form of the triphenylmethyl radical (2). Molecular weight determinations and chemical reactivity of the product of the reaction of triphenylmethyl bromide with silver suggested that hexaphenyl ethane was not a stable compound but that it existed in equilibrium with its dissociation product the triphenylmethyl radical.

It was not until 1929, however, that Paneth and Hofeditz (3), with their famous mirror technique, supplied the first direct evidence for the formation of alkyl radicals. Thermal decomposition of tetramethyl lead in a flow system was found to result in metallic lead deposition in the reaction zone while farther down stream a lead mirror, previously deposited, was observed to be removed resulting in regeneration of tetramethyl lead. Paneth and Hofeditz concluded that methyl radicals, formed thermally, were capable of reacting with metallic lead producing the starting material again.

Since these early experiments new techniques for producing and identifying free radicals have been developed. Free radicals may be formed in any of a large number of ways. These include (a) pyrolysis, (b) bombardment by high energy particles, (c) irradiation in the ultra-violet or higher energy region of the spectrum, (d) reaction of metals with halogen compounds, (e) neutralism of ions by electrode reactions and (f) oxidation-reduction reactions (eg. $\text{Fe}^{++} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{+++} + \text{HO}^- + \text{HO}\cdot$).

The number of methods of radical detection are just as varied and include (a) mirror techniques, (b) spectroscopy (absorption and emission), (c) electron spin resonance, (d) calorimetry, (e) mass spectrometry, (f) magnetic susceptibility measurements, and (g) chemical and low temperature trapping methods.

A monoradical is a species containing one unpaired electron and of all the radical species known mono-radicals have received by far the most attention. With only one unpaired electron a mono-radical has only one type of multiplicity, the doublet state. Also the majority of these species have been studied in their ground doublet state. The reactions of these radicals have been reviewed many times and probably most thoroughly by Steacie (4). The reactivity of mono-radicals is generally characterized by the following types of chemical reactions (a) abstraction, (b) recombination, (c) disproportionation, (d) isomerization and (e) decomposition.

A radical having two unpaired electrons on the same atom, unlike a mono-radical, can exhibit two types of multiplicity; it can be either a triplet or a singlet. Generally, although not always, the

triplet state is the ground state while for the same electronic configuration the Pauli principle allows two excited singlet states. Early investigators believed that these biradicals exhibited reactivities similar to mono-radicals (4). The last decade, however, has shown that species such as CH_2 , O, NH, S, Se, C atoms and substituted carbenes show reactivity that is characterized by the electronic state (multiplicity) of the biradical. For this reason mainly, the term biradical has been abandoned in favor of triplet and singlet states. The chemistry of the above species will be reviewed and it will become convincingly clear that their chemistry is indeed that of spin state reactions.

Methylene Chemistry

The chemistry of carbenes, divalent carbon species, has received an enormous amount of attention in the last decade and the subject is well reviewed in a recent book (5). The simplest carbene, methylene, has itself been the center of much work and is the subject of many good review articles (5, 6, 7). Only its salient features will be given here.

The most common sources of methylene are the photolysis and sensitization of diazomethane and ketene (8, 9).

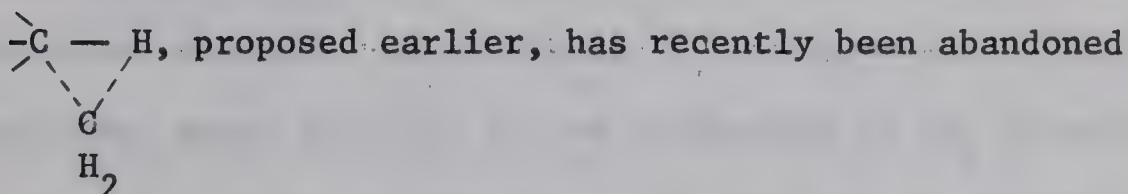
The spin state of ground state methylene was unknown until 1959 when Herzberg (10, 11), after 17 years work, obtained spectra of both the lowest singlet and triplet states. Observations showed that since the singlet decays to the triplet, the latter must have the lower energy content. As would be expected, from spin conservation

considerations, Herzberg and Shoosmith (10) observed that photolysis of diazomethane produced methylene in its first excited singlet state. No experimental measure of the energy difference between the ground and first excited state is available although it is thought to be small.

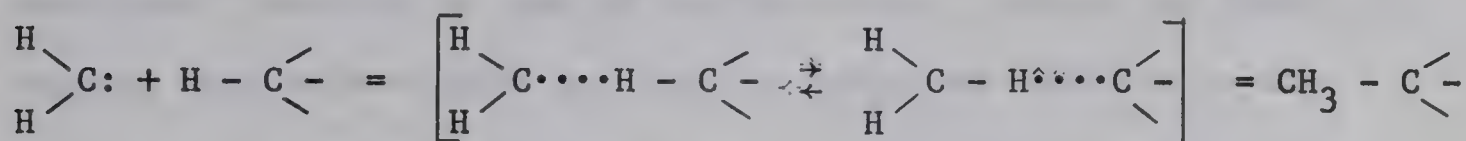
The insertion of CH_2 into C-H bonds was first reported by Meerwein, Rathjen and Werner (12), who observed all the products expected from insertion into the C-H bonds of ethers. In 1956 Doering, Buttery, Laughlin and Chaudhuri (13) reported that methylene inserts indiscriminately into the C-H bonds of n-pentane and 2,3-dimethylbutane. Richardson et al (14) studied the reaction of CH_2 with C_7 , C_8 , and C_9 alkanes and reported totally random reaction, thus indicating that methylene reacts in the first excited singlet state. Although reactions of methylene in the liquid phase exhibited a random behavior, reactions in the gas phase were found to be somewhat selective, the reactivity showing an apparent increase for secondary and tertiary bonds. Frey and Kistiakowsky (15) found the reactivity for secondary C-H bonds over primary to be 1.7 and increased with added inert gas. Richardson et al (14) suggested that the selectivity was due to triplet methylene, resulting from the decay of the originally formed singlet, and that the initial interaction was H-atom abstraction followed by radical recombination. Gaspar and Hammond (16) suggested that the increased selectivity might be due to removal of the excess energy of the methylene and would not necessarily involve the triplet state. Frey (17), using O_2 to remove products formed by radical coupling, calculated that, in the gas phase, 22% of the reaction proceeds by H-atom abstraction.

Whether the increase in discrimination is due to triplet or thermalized singlet or both, it is generally agreed that singlet methylene inserts into C-H bonds while triplet undergoes an abstraction reaction.

The three-centered transition complex for the insertion reaction



by DeMore and Benson (7) in favor of a new reaction path:



Attack by methylene on a hydrogen atom leads to an intermediate which is equivalent to the recombination complex for radicals $\text{CH}_3\cdot$ and $\cdot\text{C}\equiv$. Such a mechanism would require that these reactions depend only on energetics and are not influenced by the spin state of the carbene.

Methylene has been reported to react with olefins by insertion into alkyl and vinylic C-H bonds and by addition across the double bond. Photolysis of diazomethane in liquid cyclohexene produced the following products: norcarane 40%, 3-methylcyclohexene 25%, 4-methylcyclohexene 25% and 1-methylcyclohexene 10% (18), indicating nearly indiscriminate attack on the C-H bonds. Addition to the double bond of olefins results in formation of hot cyclopropanes which, if not stabilized, undergo isomerization or decomposition.

Skell and Woodward (19) suggested that the chemical characteristics of singlet and triplet methylene were different. They reasoned that singlet methylene would add to the double bond in a spin allowed single concerted step thus retaining geometric configuration of the reactant molecule. Conversely, they argued that triplet addition would require initial formation of a triplet biradical which, due to rapid rotation of the intermediate, would destroy the original config-

uration. Much data has since been compiled, most of which is not in disagreement with these original ideas. Photolysis of diazomethane with either cis or trans-2-butene in both liquid and gas phase has resulted generally in retention of configuration (20, 21). Addition of inert gases (22, 23, 24) or production of CH_2 by mercury photosensitization of diazomethane (25) (thought to produce triplet methylene) resulted in loss of configuration. Benson and DeMore (7) suggest that both singlet and triplet methylene addition to the double bond results in formation of an intermediate biradical and kinetic parameters involving rotation vs. ring closure are responsible for configuration of the products. Gaspar and Hammond (16) disagree, arguing that stereospecific addition demands simultaneous formation of two bonds (ie. singlet addition), while conversely, non-stereospecific addition cannot be taken as proof that the attacking species is a triplet. It would appear now, in light of recent work with sulfur atoms, that configurational analysis alone is insufficient to determine the spin state of the reacting species (26).

Reactions of methylene with the triple bond have received little attention. Sakai and Shida (111) observed that the reaction of methylene with acetylene, in the gas phase, gave methyl acetylene and allene in a constant ratio of 1.5 ± 0.3 . The products were thought to arise from isomerization of a hot cyclopropene intermediate. No cyclopropene was found as a product, probably due to the high exothermicity of the reaction and the instability of the cyclic product.

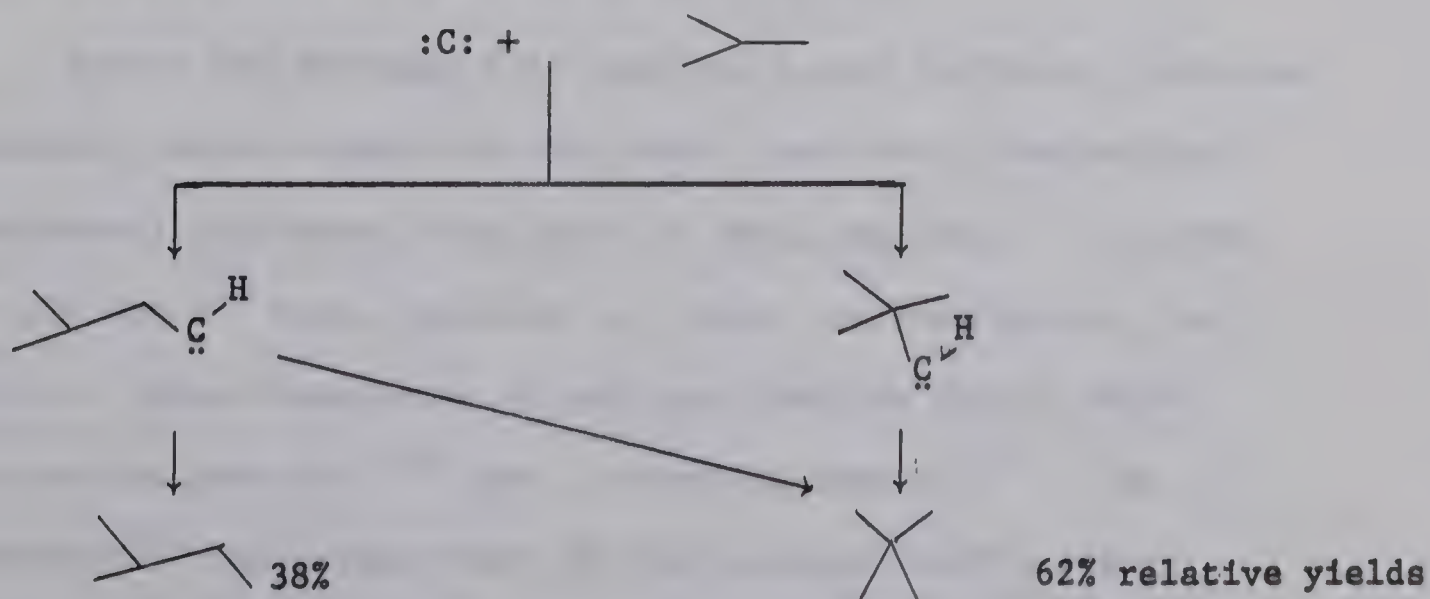
Jacox and Milligan (65) found allene as the only photolysis product of dilute solid solutions of $\text{CH}_2\text{N}_2 + \text{C}_2\text{H}_2$ in argon at 4 K. No

cyclopropene was formed under these conditions.

Carbon Atoms

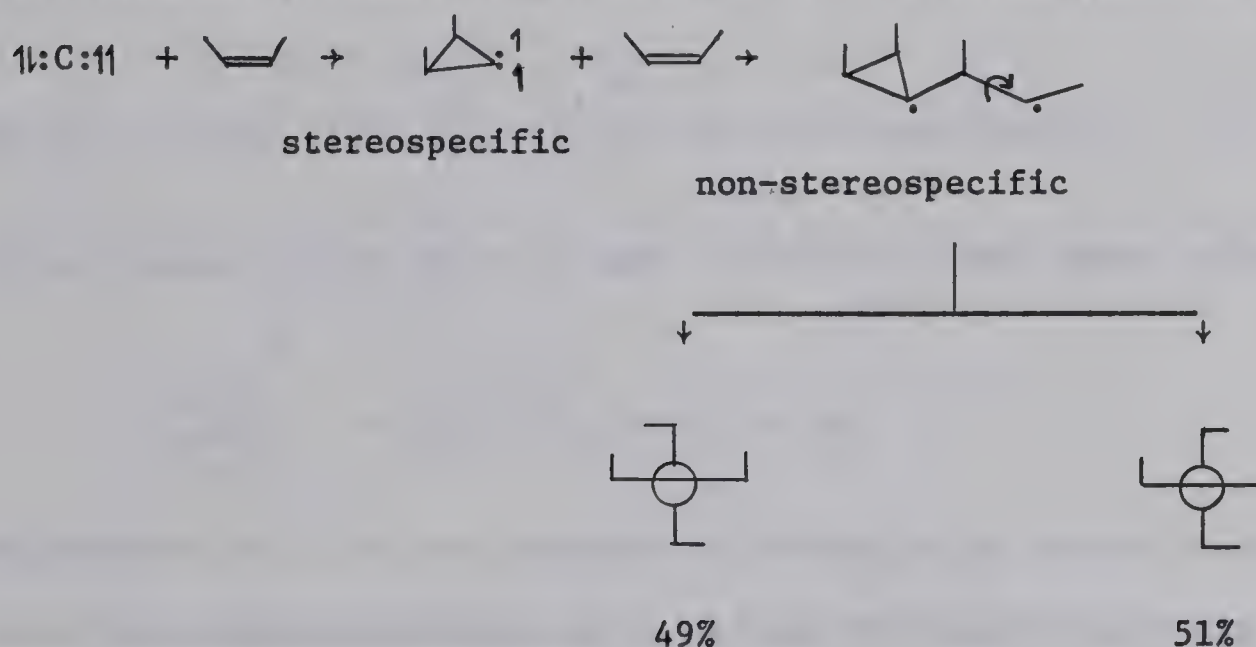
Skell and Engel have observed the reactions of carbon atoms in their three low lying states; 1S , 1D and ground 3P (27, 28, 29, 30). Carbon vapor, generated by a carbon arc, deposited in paraffin hydrocarbon matrices shows no diminution of C_1 or C_3 content after remaining at $-196^\circ C$ for several hours. By chemical means, from product analysis, Skell and Engel calculated the half-life of the two metastable states, in the matrix at $-196^\circ C$, to be 2 seconds for $C(^1S)$ and 15 seconds for $C(^1D)$. Reactants could be deposited in the cell simultaneously with deposition of carbon vapor or at any time after. This time-delay technique enabled elucidation of the reactivities of the three carbon species.

The reaction of carbon atoms with isobutane yielded 1,1-dimethylcyclopropane and 2-methylbutane as the major products. The initial reaction is postulated to be an insertion into either primary or tertiary C-H bond followed by intramolecular insertion or H-atom abstraction by the intermediate carbene:

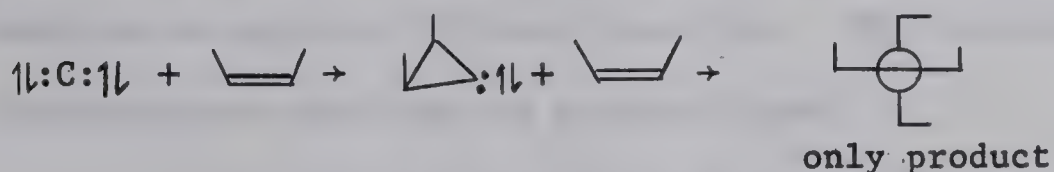


The time-delay technique determined that all the products resulted from reactions of the 1S state of carbon. Studies where only 1D and 3P atoms were present resulted in no products.

Triplet ground state carbon atoms react with cis and trans-2-butene forming spiropentanes as the only products. Isomeric distribution of products indicate that ring formation by the stereospecific mode precedes ring formation by non-stereospecific mode.



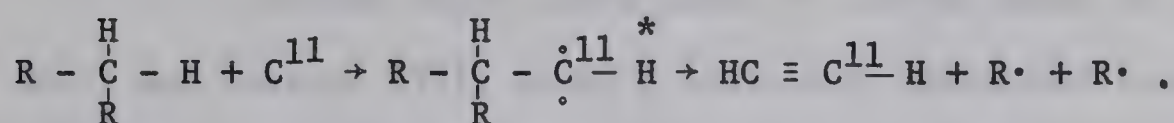
Carbon atoms in the 1D state react with cis-2-butene to give the substituted spiropentane by two stereospecific additions:



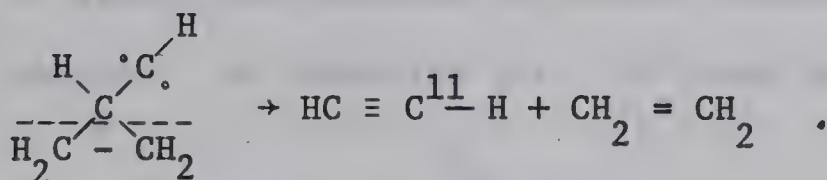
MacKay and Wolfgang (31) employed a very different technique for producing carbon atoms with the result that their observations are considerably different from those of Skell and Engel. A pulsed beam of 120 Mev C^{12} ions, provided by a heavy ion accelerator, was focused on a target consisting of gold and platinum foils, which strip a neutron from the C^{12} ions, converting them to C^{11} . The newly formed C^{11} ion retains most of its original kinetic energy and enters the reaction vessel through a brass foil. The C^{11} ion

must be cooled to below 100 ev before it can react chemically as a neutral atom; the resonance rule predicts that the atom will be in a low-lying electronic state, probably the ground 3P state.

The major product in the reaction of C^{11} atoms with alkanes is acetylene. The initial interaction is described as an insertion into a C-H bond followed by decomposition of the hot carbene intermediate:



Cyclopropane yields twice as much acetylene as any other hydrocarbon:



Decomposition of the hot carbene is particularly favored in this case since stable products can be formed by simple electronic rearrangement with little nuclear motion.

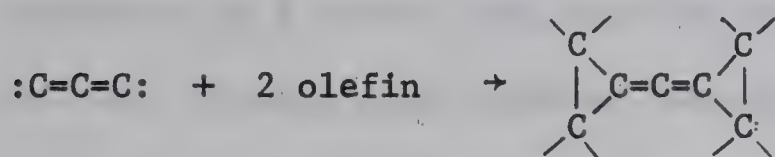
Reactions of C^{11} atoms with alkenes results in π -bond addition as well as C-H bond insertion. The cyclopropylidene intermediates rearrange to yield allenes.

Addition of inert gas moderators decreased the yield of acetylene and reactions in the liquid phase further reduced this product; acetylene must therefore arise from decomposition of hot intermediates. The reaction of thermal carbon atoms with ethylene in rare gas matrices (32) resulted in a low yield of acetylene, although not complete elimination of this product, but unlike Skell's results did not produce any spiropentane.

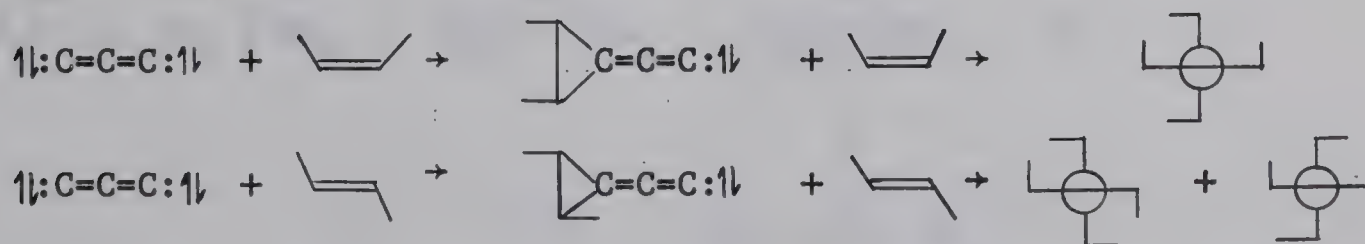
Although the results of Skell and Wolfgang approach each

other, under similar conditions of low temperature solid phase reactions of thermal carbon atoms, considerable differences still exist. These differences can be resolved only if it is assumed that reactions of recoil carbon atoms, even in the solid at low temperatures, produce hot reaction intermediates which contain more excess energy than those produced by the reaction of carbon atoms in paraffin matrices at -196°C .

A second major constituent of carbon vapor is C_3 , dicarbene. Skell and Wescott (33), using a previously described time-delay technique, observed that C_3 , deposited on a hydrocarbon matrix at -196°C , reacts with olefins to produce bisethanoallenes as the only products. No insertion into C-H bonds occurs.



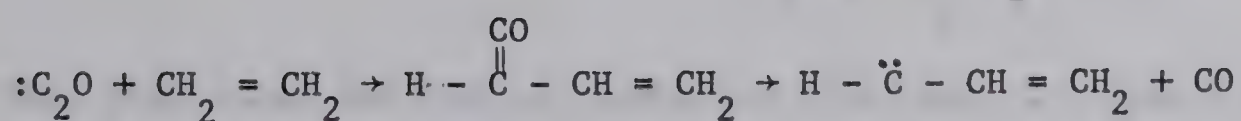
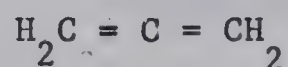
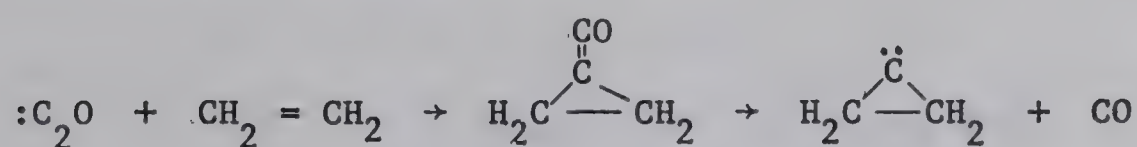
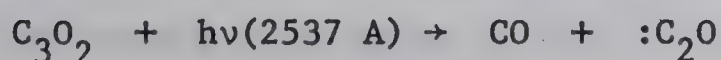
Analysis of the spectrum of C_3 (34) and theoretical calculations (35) indicate that dicarbene is singlet in the ground state. Results with cis and trans-2-butene are consistent with singlet dicarbene:



Isomeric product distribution shows that dicarbene adds to the double bond in two stereospecific steps. When the olefin and C_3 were deposited on the hydrocarbon matrix simultaneously a fourth product was formed with both cis and trans-2-butene. Geometry of this product indicated that the reaction path consisted of one stereospecific and one non-stereospecific step. Skell and Wescott

concluded that C_3 , in a triplet metastable state, is produced in the carbon arc by electron bombardment of C_3 . They argued that excess vibrational energy in the initially formed dicarbene would be lost rapidly and non-stereospecific addition is due to triplet C_3 rather than isomerization of the initial hot adduct. Simultaneous deposition of carbon vapor and olefin could, however, result in reaction in the gas phase before the reactants reached the hydrocarbon matrix, thus eliminating matrix stabilization.

Bayes (36, 37, 38) photolyzed carbon suboxide in the presence of ethylene, methane and cyclopropane and observed products similar to those found in carbon atom reactions. Allene and methylacetylene were formed in the C_3O_2 -ethylene system suggesting insertion of a carbon atom into C=C and C-H bonds. Energetically, however, formation of a carbon atom from photolysis of C_3O_2 at 2537 Å is impossible; the reacting species is therefore probably $:CCO$.

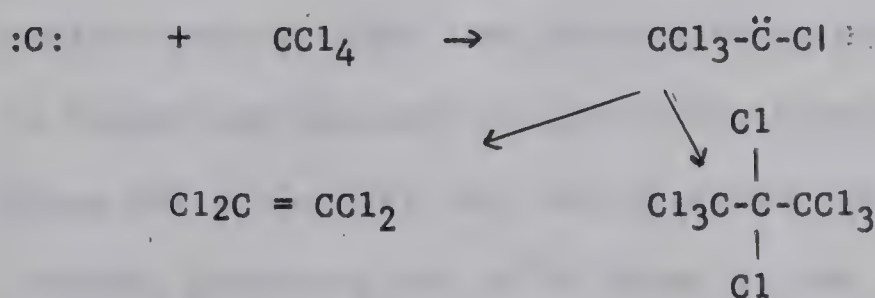


Photolysis of C_3O_2 with methane yielded ethylene but no acetylene (36), further suggesting that carbon atoms are not the reactive species.

Mullen and Wolf (39) photolysed Carbon-2-C¹⁴-Suboxide in ethylene and observed the isotopic distribution in the allene to be 92% C¹⁴ in the central carbon position. Allene is therefore formed mainly by addition of C₂O to the double bond and not by insertion into the C-H bond followed by isomerisation.

Acetylene and ethylene are found as products of the photolysis of carbon suboxide with methane at 1470 Å (40), whereas photolysis at 2537 Å results only in ethylene (36). Stief and DeCarlo (40) conclude that while :C₂O is the reactive species at 2537 Å, carbon atoms are produced in the vacuum u.v. region. Energetically C(¹D) atoms could be formed from the 1470 Å (E = 195 kcal/mole) photolysis of C₃O₂. Secondary photolysis of ethylene has been eliminated as the source of acetylene in the short-wavelength region (40, 41).

Skell and Harris (112) have recently investigated the reactions of carbon atoms with chlorinated hydrocarbons. The reaction of carbon atoms with carbon tetrachloride yielded two products, tetrachloroethylene and octachloropropane.



They postulated the initial reaction to be insertion into a carbon-chlorine bond forming trichloromethylchlorocarbene as the intermediate. This intermediate can either stabilize by chlorine rearrangement, producing tetrachloroethylene, or can insert into the carbon-chlorine bond of a second carbon tetrachloride molecule, producing octachloro-

propane. Reaction occurs from 1S and 1D states of atomic carbon but not from the 3P ground state.

The reaction of carbon atoms with t-butyl chloride produces 1-chloro-2, 2-dimethylcyclopropane as the major product. This is postulated as an initial insertion into the carbon-chlorine bond forming t-butylchlorocarbene as the intermediate, followed by intramolecular insertion into a β -carbon-hydrogen bond. 2-chloro-3-methylbutene-2 is produced as a minor product; this could result from a methyl shift.

Oxygen Atoms

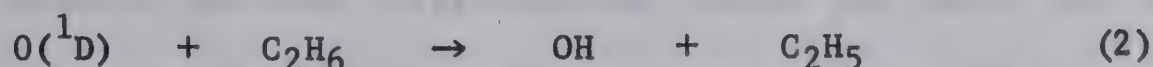
Early investigations of the reactions of oxygen atoms did not specify the electronic state of the atom, but simply referred to these systems as O-atom reactions.

Harteck and Kopsch (42), using an electrical discharge in oxygen, studied the reactions of oxygen atoms with a variety of compounds including some paraffins. The initial interaction was suggested to be a hydrogen abstraction:



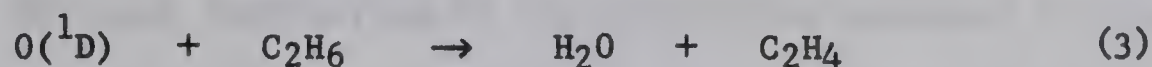
This was probably true in this case since O-atoms produced by electrical discharge in oxygen are probably formed in their ground 3P electronic state.

Noyes and co-workers (43, 44) observed the reactions of $O(^1D)$ atoms with ethane, producing the $O(^1D)$ atoms by the photolysis of nitrous oxide. Many of the observations were explained by proposing an initial hydrogen abstraction:



Ethyl alcohol was found to be a major product, but since its yield, in the presence of an atom scavenger, iodine, was zero it was suggested

that it was not formed by a direct reaction between oxygen atoms and ethane. The results favored the recombination of hydroxy and ethyl radicals. The production of ethylene decreased in the presence of iodine but failed to reach zero, the value expected if it originated from the disproportionation of ethyl radicals. A reaction, involving no alkyl radicals, was introduced to account for the residual ethylene:

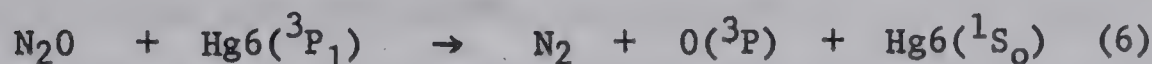
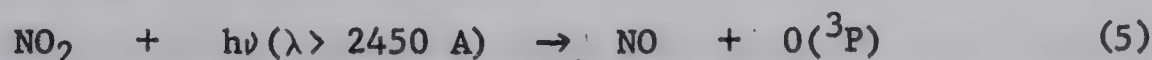


Secondary reactions were found to be very important in this system and indeed hindered the elucidation of the primary reactions.

In a more recent study, Wright (45) has investigated the reactions of $\text{O}(^3\text{P})$ atoms with isobutane. The oxygen atoms were produced by the NO titration of N atoms described by Kaufman and Kelso (46). The reaction is believed to give ground state oxygen atoms by the reaction:

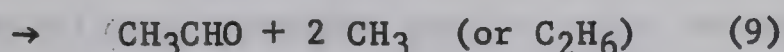
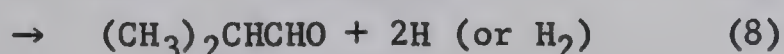
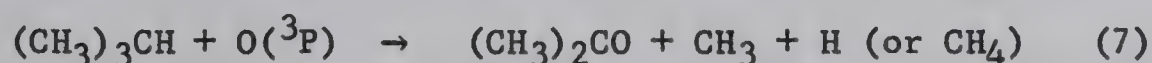


Triplet oxygen atoms were also produced, in static systems, by the photolysis of NO_2 with light of wavelength greater than 2450 Å (47) and by the mercury-photosensitized decomposition of nitrous oxide described by Cvetanovic (48). Both systems are known to give oxygen atoms in their ground electronic state by the following reactions:



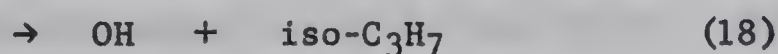
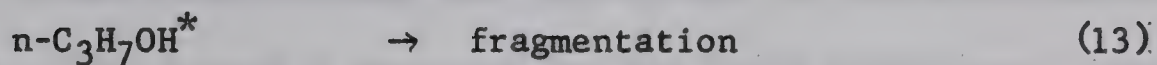
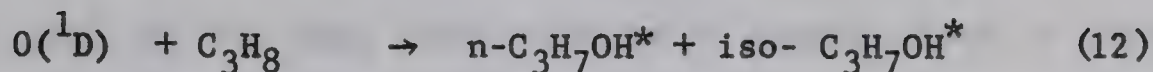
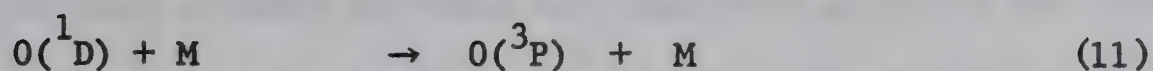
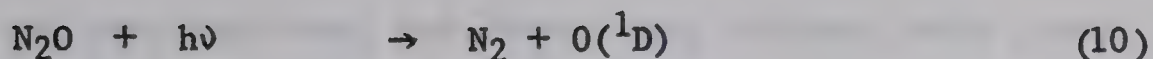
The main products and their distributions, using the latter two sources of oxygen atoms, were essentially the same as found in the titration technique. This was taken as added evidence that oxygen atoms generated

by the reaction of N atoms with NO, are indeed in their ground electronic state. The ratio tert-BuOH/acetone was found to be 0.2 which is 100 times smaller than that expected if tert-butoxy radicals had been the common precursor to the two products. The product ratio was also found to be independent of total pressure, indicating that hot tert-butoxy radicals were not responsible for the large yield of acetone. Hydrogen abstraction by the oxygen atom appeared to play only a minor role and product formation was thought to arise by a more direct manner involving the simultaneous replacement by an oxygen atom of two groups on the parent hydrocarbon.



In a later study, employing the mercury-photosensitised decomposition of nitrous oxide, Woods et al (49), have shown that in the reaction of $\text{O}(^3\text{P})$ atoms with isobutane the primary step is indeed hydrogen atom abstraction by the oxygen atom. Product analysis indicates that abstraction of the tertiary hydrogen is preferred.

Yamazaki and Cvetanovic (50), generating oxygen atoms by the photolysis of nitrous oxide, have provided the most illuminating study of oxygen atoms to date. Three major processes have been elucidated in the reactions of $\text{O}(^1\text{D})$ and $\text{O}(^3\text{P})$ atoms with propane: (a) random insertion of $\text{O}(^1\text{D})$ atoms into C-H bonds, (b) abstraction of hydrogen by $\text{O}(^3\text{P})$ atoms, and (c) pressure dependent fragmentation of the initially produced hot insertion products. The reaction of $\text{O}(^1\text{D})$ atoms closely parallels the insertion reactions known for $\text{S}(^1\text{D})$ (51) and $\text{CH}_2(^1\text{A}_1)$ (7).



When gases capable of deactivating the excited oxygen atoms are added, the insertion and fragmentation decrease and the secondary hydrogen atoms are preferentially abstracted. From the increased discrimination in hydrogen abstractions, the following relative rates for the electronic deactivation of the excited singlet oxygen atoms by different gases have been obtained: Xe 0.47, N₂ 0.15, Kr 0.05 and He and SF₆ close to zero.

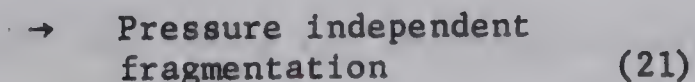
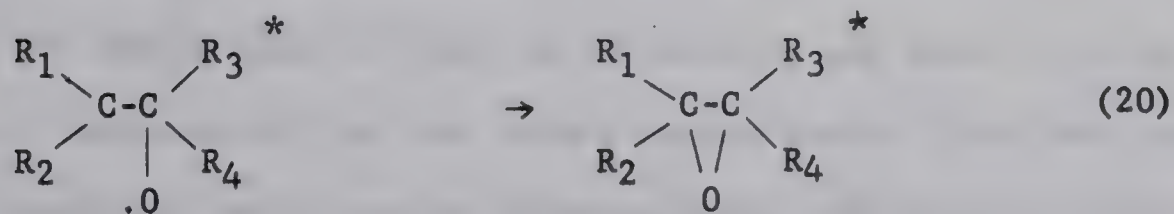
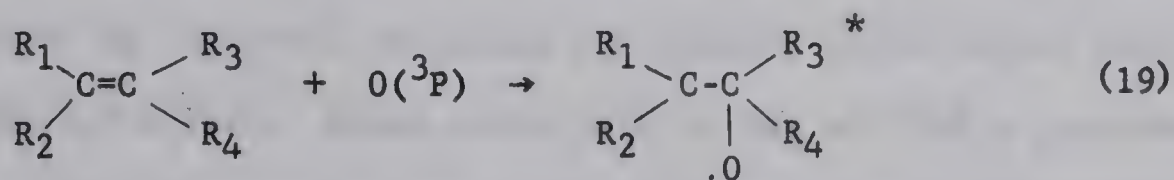
The reactions of oxygen atoms with olefins have been studied by two independent groups of workers; Avramenko and Kolesnikova (52) and Cvetanovic (53). Avramenko and Kolesnikova used the electrical discharge through molecular oxygen and water vapor to generate oxygen atoms. From their studies they drew the following conclusions: (a) an oxygen atom is capable of breaking the carbon-carbon double bond with formation of an aldehyde, (b) during the rupture of the double bond the larger aldehyde is preferentially formed and (c) insertion into

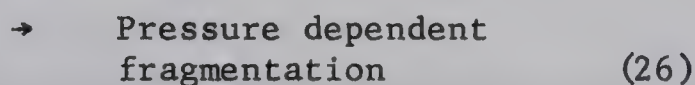
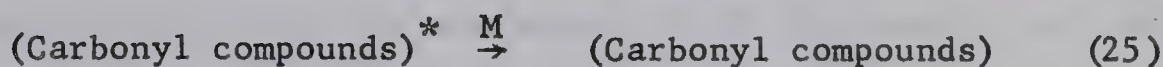
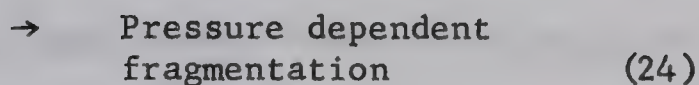
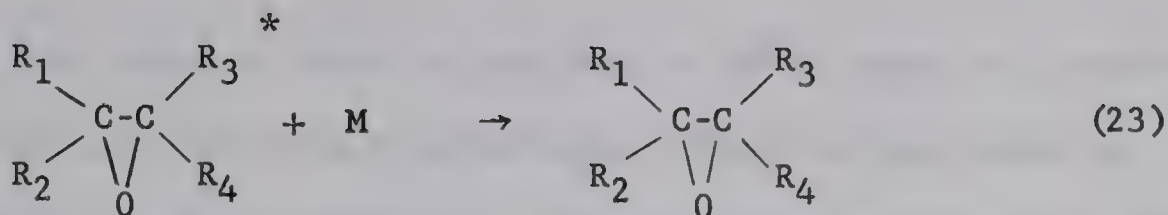
C-H bonds at both saturated and unsaturated carbons takes place. They observed not only primary products but secondary products and also products arising from the participation of two oxygen atoms. The low pressures used and the high concentration of oxygen atoms in the system necessarily add complications and limitations to this experimental technique. This probably accounts for the large differences observed by Cvetanovic for the reactions of oxygen atoms with olefins.

Cvetanovic and co-workers have thoroughly studied the reactions of $O(^3P)$ atoms with olefins and their investigations have recently been reviewed (53). Photochemical methods have been used almost exclusively for the generation of oxygen atoms, the most commonly used source being the mercury-photo sensitized decomposition of nitrous oxide. The spin conservation rule requires that the oxygen atom be formed in the ground electronic state;



The spin rule also requires that the reaction of $O(^3P)$ with an olefin results in an initially formed triplet biradical. The following reactions have been postulated to account for the observations:





The following additional features were observed in these reactions:

(1) Addition of $\text{O}(^3\text{P})$ to the double bond is non-stereospecific. This is evident from the fact that starting with either cis or trans-2-butene both cis and trans-2-butene oxide were formed.

(2) The oxygen atom adds to the least substituted carbon atom.

(3) Internal rearrangements of the initial biradicals occur producing aldehydes and ketones.

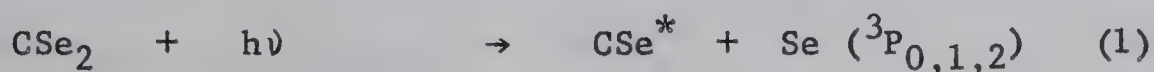
Photolysis of NO_2 , in the region 4047-2537 Å, exhibited all the features of the olefin reactions with oxygen atoms produced by the N_2O technique. The photolysis of NO_2 at 2288 Å, in the presence of butene-1, resulted in an increased yield of epoxide relative to n-butyraldehyde. Increasing amounts of N_2 , however, decreased the epoxide yield to the same value found in the N_2O system. Since photolysis of NO_2 at 2288 Å generates $\text{O}(^1\text{D})$ atoms, this observation was taken to suggest that $\text{O}(^1\text{D})$ atoms react with the double bond to form the epoxide in one step, i.e., by the simultaneous formation of the two carbon-oxygen bonds. This one step addition, therefore, must require stereospecific addition of $\text{O}(^1\text{D})$ to the double bond. Attempts to verify this using cis and trans-2-butene were not conclusive due to the large reactivity of β-butene oxides with NO_2 .

The relative rates of addition of $O(^3P)$ atoms to a series of olefins (53) have definitely established triplet oxygen atoms as electrophilic reagents (Table I). The relative preexponential factors were found to be constant within experimental error indicating the differences in reactivity are due mainly to differences in activation energies.

Haller and Pimentel (54) report that photolysis of N_2O at 1470 Å in the presence of acetylene in an inert matrix at 20K resulted in the formation of ketene. They suggested that the ketene is formed by the addition of $O(^3P)$ to the acetylene followed by rearrangement of the adduct.

Se Atoms

Recently Callear and Tyerman (55, 56) have reported the reactions of atomic selenium with olefins. Atomic selenium was produced by the isothermal flash photolysis of carbon diselenide which was shown to proceed by two paths:



Approximately 20% of the CSe_2 dissociates and the remainder is excited to metastable states (57). Initially the Se atoms are electronically hot, but they are rapidly deactivated by N_2 to their equilibrium distribution among the 3P states.

After the flash, atomic selenium persists for ca. 10^{-4} sec., its spectrum is then replaced by that of Se_2 . If olefins are added to the system the Se spectrum disappears more rapidly, no Se_2 is observed, and new band systems corresponding to a new product appear. Identical

TABLE I

RELATIVE RATES OF ADDITION OF $S(^3P)$, $O(^3P)$ and $Se(^3P)$
ATOMS TO OLEFINS

Olefin	$O(^3P)^a$	$Se(^3P)^b$	$S(^3P)^c$
ethylene	1.00	1.00	1.00
propylene	5.75	2.6	6.9
<u>trans</u> -butene-2	28.3	56	20
<u>cis</u> -butene-2	23.8	23.9	16
1-butene	5.75	7.1	10
isobutylene	15.0	44.7	50
pentene-1	-	5.0	10
2-methyl-butene-1	-	-	56
cyclopentene	29.8	-	18

a). ref. (53)

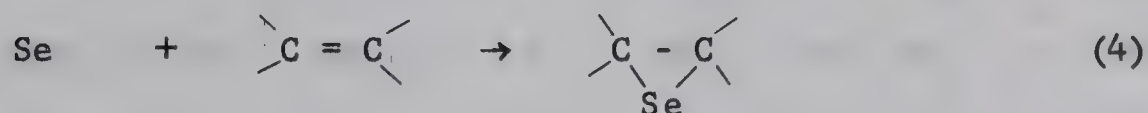
b). ref. (55)

c). ref. (77)

bands appear when carbon oxyselenide (COSe) is flash photolysed in the presence of olefins. In this case the spin conservation rule requires that the selenium atom be produced in the singlet state:



These new bands have been assigned to cyclic selenides formed from the reaction of selenium atoms with olefins:



Relative rate constants for the reaction of atomic selenium with olefins have been determined by monitoring the intensities of the ethylene selenide spectra produced after photolysis of a CSe₂-ethylene-olefin mixture. The results, given in Table I, show the trend in reactivity is similar to that found for O(³P) and S(³P) atoms. They concluded Se(³P) is also an electrophilic reagent. Temperature studies have shown that the Arrhenius preexponential factors are constant within experimental error and that changes in reactivity are due solely to changes in activation energies.

Unlike epoxides and episulfides, the cyclic selenides were found to be unstable compounds. Ethylene selenide, for example, completely disappears after ca. 100 seconds.

NH Radicals

Although the simplest member of the imidogens, the NH radical, has been known for many years, the reactivity of the NH radical is still in doubt.

Hydrogen azide (HN₃) and isocyanic acid (HNCO) are the most common sources of imidogen. The photolysis and mercury-photosensitized

decomposition of hydrogen azide have been studied by Beckman and co-workers (58, 59) who showed that the decomposition had a quantum yield of about 3. Thrush (60) observed the $A^3\Pi \leftarrow X^3\Sigma^-$ absorption band of triplet ground state NH in the flash photolysis of HN_3 . He proposed the following mechanism for the photolysis of hydrogen azide:

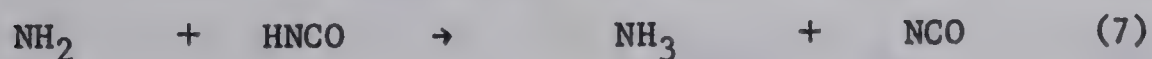
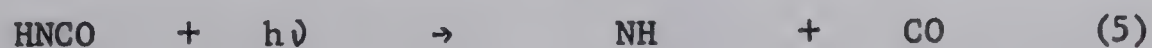


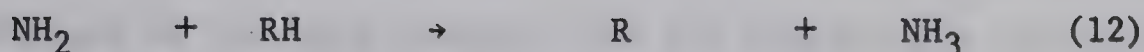
The spin conservation rule requires that NH be formed initially in an excited singlet state. Two low lying singlet states exist for NH, $^1\Delta$ and $^1\Sigma^+$, having energies of 27 and 55 kcal./mole respectively above the $^3\Sigma^-$ ground state (61).

The NH radical is isoelectronic with CH_2 , O, S, Se etc., and would be expected to undergo insertion and addition reactions.

Miller (62) studied the reaction of the NH radical in the gas phase at room temperature with a number of paraffins. There was significant attack of the NH on hydrocarbons larger than C_2 to produce amines. No reaction mechanism was concluded although C-H insertion was suggested.

Brash and Back (63), using HNCO, observed the reactions of NH radicals with paraffins and suggested the following sequence of reactions to account for the results:

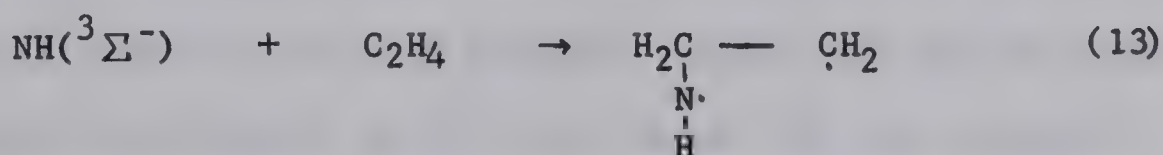




No amines or other nitrogenous compounds were detected and the mechanism suggested involves the decomposition of short lived vibrationally excited amines formed by insertion of NH radicals into C-H bonds.

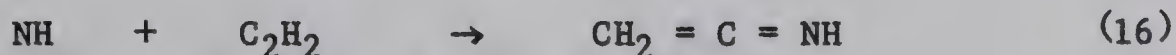
Addition of a hydrocarbon decreased the CO yield to $R^0(\text{CO})/3$, where $R^0(\text{CO})$ is the yield of CO formation in the absence of any hydrocarbon. This would indicate that all the NH radicals formed in reaction 5 were completely scavenged. The main product formed in the HNCO-propane system was 2, 3- dimethylbutane from the recombination of isopropyl radicals.

Cornell et al (64), using the technique of kinetic flash photolysis, have recently shown that the reaction of NH with ethylene, in the gas phase, results in the formation of HCN, CH_4 , CH_3CN , H_2 and an unidentified solid. Absorption spectroscopy showed that the photolysis of HN_3 resulted in the production of ground state NH ($^3\Sigma^-$) radicals exclusively; no $\text{NH}(^1\Delta)$ or other singlet species could be detected. The products are explained in terms of the reaction of $\text{NH}(^3\Sigma^-)$ radicals with ethylene.



The ethylimidogen intermediate is supported by the photolysis of ethyl azide which gave the same products as the $\text{HN}_3\text{-C}_2\text{H}_4$ system. The total cyanide yield represents 10% of the HN_3 consumed, the major reaction being formation of a solid. No ethylene imine was detected. A rough estimate of the rate constant for the bimolecular addition of $\text{NH}({}^3\Sigma^-)$ to C_2H_4 is 10^7 l/mole-sec.

Jacox and Milligan (65) obtained ethylene imine as the only product from the photolysis of $\text{HN}_3 + \text{C}_2\text{H}_4$ in argon at 4° K. Evidence also suggests the production of ketenimine by the analogous reaction of NH with C_2H_2 .



Sulfur Atoms

The photolysis of carbonyl sulfide provides a clean source of sulfur atoms and recently the reactions of sulfur atoms have been studied by Gunning and co-workers (66). The U. V. spectrum of COS consists of a banded spectrum between 2600 Å and 2000 Å with a maximum at 2235 Å. From the integrated absorption coefficients Sidhu et al (67) calculated the lifetime of the upper state to be 10^{-9} sec. and from semi-empirical M.O. calculations they indicate the first excited state of COS corresponds to a $\pi \rightarrow \pi^*$ transition.

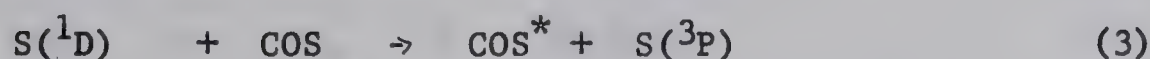
Recent studies have employed three different light sources for the photolysis of COS and in each case the energy of the initially-formed sulfur atom has been well defined. Taking the heat of formation of ground state sulfur as 66.0 kcal./mole (68) and $\Delta H_f(\text{COS}) = -33.8$ kcal./mole (69) the bond energy $D(\text{OC}=\text{S}) = 72.4$ kcal./mole. The first excited singlet state of the S atom is 26.4 kcal./mole above

the ground state (76), thus the spin allowed dissociation



requires a photon having a minimum energy of $72.4 + 26.4 = 98.8$ kcal./mole corresponding to a wavelength of 2895 Å. Assuming equipartition of excess energy between the CO and the S atom, the three light sources generate sulfur atoms having varying translational energies. The energy required to produce a sulfur atom in the next highest singlet state would require $72.4 + 63.4 = 135.8$ kcal./mole corresponding to a wavelength of 2105 Å.

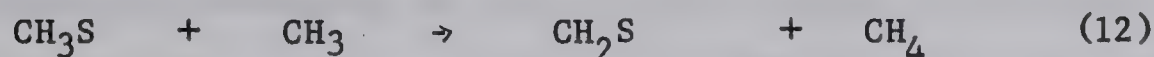
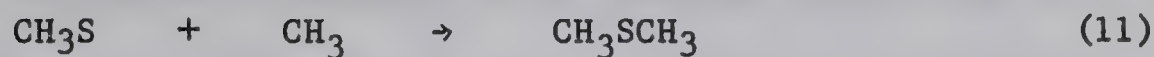
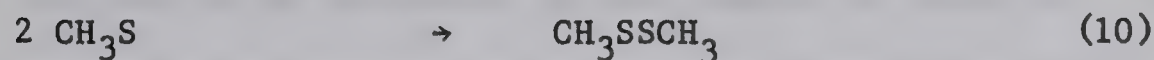
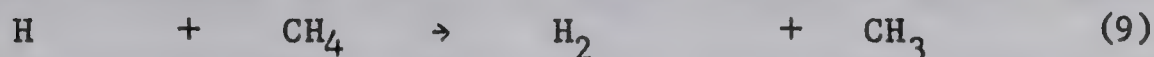
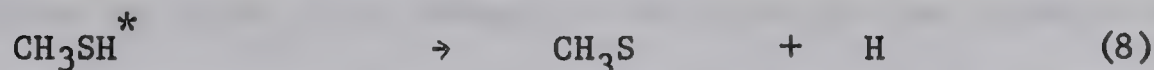
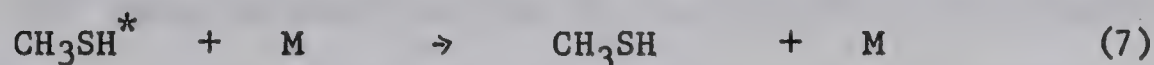
The mechanism proposed for COS photolysis is:



COS is efficient in bringing about electronic relaxation of $\text{S}(^1\text{D})$ to the ground state (70). Reaction 5 is essentially zero since the CO formation is reduced to $R^0(\text{CO})/2$ upon addition of a substrate which will completely scavenge the initially produced sulfur atoms (71). The observed quantum yield of 1.80 is lower than the expected value of 2.0 (67) but since the observed quantum yield is independent of pressure this effect suggests an inefficiency in the photolytic dissociation which may arise from radiative or non-radiative transitions to the ground state.

The photolysis of COS-paraffin mixtures has resulted in the following observations:

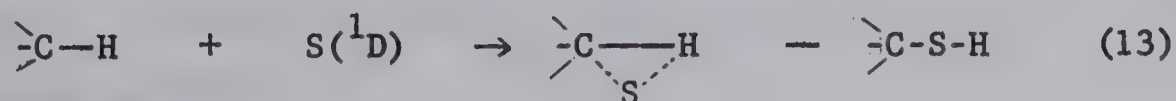
(a). The major products of the reactions are the corresponding mercaptans. No H_2S or other hydrocarbons were formed, the only exception being methane where decomposition of the initially-formed mercaptan occurred to a large extent. The exothermicities of the S atom reactions are approximately 85 kcal/mole and, with the exception of methane, the vibrational degrees of freedom are sufficient to stabilize the initially-formed hot mercaptans. Product analysis of the methane reaction indicates the following reactions:



The ratio $\text{CH}_3\text{SH}/\Sigma \text{CH}_3\text{S} = 0.67$ was independent of total pressure up to 1450 torr indicating that one third of the hot methyl mercaptan underwent pressure-independent fragmentation.

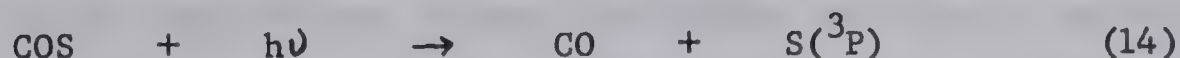
The exothermicity of the reaction of sulfur atoms with cyclopropane was insufficient to bring about rearrangement of the initially-formed hot product as cyclopropyl mercaptan was the only product formed.

In view of the product formation, a direct insertion of the sulfur atom into the C-H bond of the paraffin has been proposed as the reaction path:



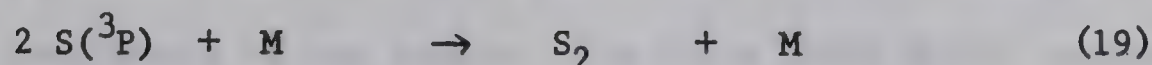
(b) The rate of reaction of the sulfur atoms with C-H bonds does not depend on the type of bond, as is generally observed in abstraction reactions, but shows equal preference for primary, secondary and tertiary C-H bonds. With propane and isobutane, the isomeric distribution of mercaptans, $n\text{-PrSH}/i\text{-PrSH} = 2.85 \pm 0.05$ and $i\text{-BuSH}/t\text{-BuSH} = 8.8 \pm 0.1$, demonstrates the indiscriminate attack on C-H bonds (72). This parallels the reactions of singlet methylene as first observed by Doering *et al* (13).

(c) When carbonyl sulfide is photolysed in the presence of a paraffin the rate of CO formation decreases as the pressure of the paraffin increases but fails to reach a value $R^0(\text{CO})/2$, where $R^0(\text{CO})$ is the rate of CO formation in the absence of paraffin. Instead, it approaches a constant value somewhat larger than this indicating incomplete scavenging of the initially formed sulfur atoms. The addition of a large excess of CO_2 reduces the mercaptan yield to zero (72). Since CO_2 is inert towards sulfur atoms it acts only in efficiently bringing about electronic relaxation of the $\text{S}(^1\text{D})$ atoms to the $\text{S}(^3\text{P})$ ground state. This indicates that $\text{S}(^3\text{P})$ atoms do not react with paraffins and that the $\text{S}(^1\text{D})$ atom alone is responsible for insertion into C-H bonds. The fact that, in the COS-paraffin system, the rate of CO remains above $R^0(\text{CO})/2$ indicates that deactivation of the $\text{S}(^1\text{D})$ atom occurs. It has been suggested that this effect may also arise due to the spin-forbidden dissociation of COS (73):



From the rate of mercaptan formation this process could occur to the maximum extent of 26%.

On the basis of the results, the following mechanism was proposed for the reaction of sulfur atoms with paraffinic hydrocarbons:



A steady-state treatment of the reaction mechanism yields the following expression for the rate of mercaptan formation:

$$\frac{R(\text{CO})}{2} \cdot \frac{P(\text{RH})}{R(\text{RSH})} = \frac{k_{17}}{k_{15}} \cdot \frac{P(\text{COS})}{k_{15}} + \frac{k_{15} + k_{16}}{k_{17}} \cdot \frac{P(\text{RH})}{k_{17}} \quad (20)$$

The equation yields straight lines when the data for various paraffins are plotted. The intercepts and slopes are the same for all paraffins studied giving the values of $k_{17}/k_{15} = 2.0$ and $k_{16}/k_{15} = 0.70$. The above results were obtained with a filtered medium pressure mercury arc (λ eff. = 2490 Å). Results obtained with a Cd resonance lamp (λ eff. = 2288 Å) are $k_{17}/k_{15} = 2.2$ and $k_{16}/k_{15} = 0.3$ (73). Although the ratio of abstraction to insertion is independent of wavelength, the ratio of deactivation to insertion shows a marked decrease. This was attributed to excess translational energy of the sulfur atom produced by the photolysis of COS at 2288 Å.

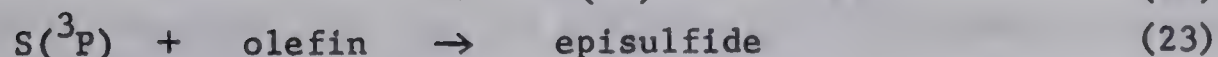
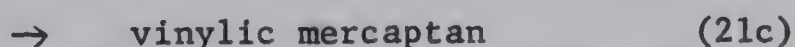
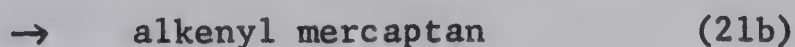
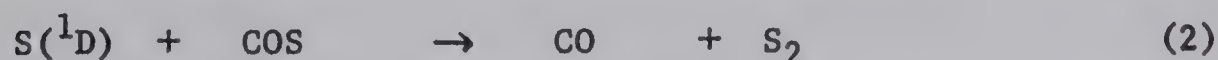
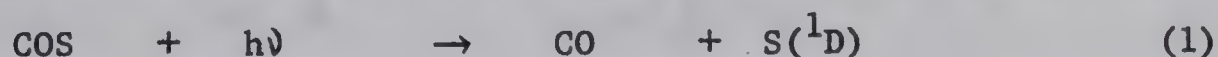
Cyclic episulfides, alkenyl mercaptans and vinylic mercaptans are products of the reaction of sulfur atoms with olefins. The value of $R(\text{CO}) - R^0(\text{CO})/2$ approaches zero within experimental error, indicating the complete scavenging of sulfur atoms by the olefin. Product yields

in terms of $R^O(CO)-R(CO)$, in low conversion runs, indicated quantitative reaction of sulfur atoms. Addition of a large excess of CO_2 suppressed the mercaptan yield showing that $S(^1D)$ atoms alone are precursors to mercaptan formation. Ground state triplet sulfur atoms react with olefins to produce only episulfides. Alkenyl mercaptans result from insertion into C-H bonds, however, vinylic mercaptans are suggested to arise from isomerization of sulfur atom addition precursors (26), as indicated by the decrease in vinylic mercaptan formation with increasing molecular complexity of the olefin. The ratio, $R(M)/R(ES)$, varies from 0.4 to 1.0 depending on the olefin, generally showing an increase with increasing alkyl substitution on the double bond. Ethylene is an exception, exhibiting the largest ratio of ca. 1.0.

Ethylene yields ethylene episulfide and vinyl mercaptan, from the photolysis of COS at 2490 Å, in the ratio $R(M)/R(ES) = 0.95$. The high pressure distribution for propylene yields 70% propylene episulfide, 15% allyl mercaptan and 15% methylvinyl mercaptan. Cis and trans-2-butene produced only traces of vinylic mercaptans.

The ratio $R(M)/R(ES)$ was found to increase when COS was photolysed at 2288 Å, and as in the paraffin case this was attributed to the excess translational energy of the sulfur atom.

The following mechanism accounts for the general observations:



Steady-state treatment of the reaction steps gave the expression:

$$\left[\frac{R(CO) - R^O(CO)/2}{R(CO)} \right]^{-1} = \frac{2}{R(CO)} + \frac{k_{21}}{k_2 + R^O(CO)/2} \cdot \frac{P(O_1)}{P(COS)} \quad (24)$$

where $k_{21} = k_{21a} + k_{21b} + k_{21c}$.

The ratio k_{21}/k_2 , however, was found to be pressure dependent, first decreasing to a minimum and then increasing, with increasing olefin pressure. This effect was thought to be due partly to an additional $S(^3P)$ forming step:

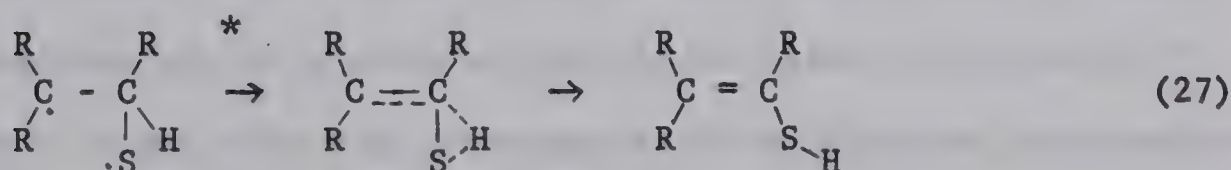
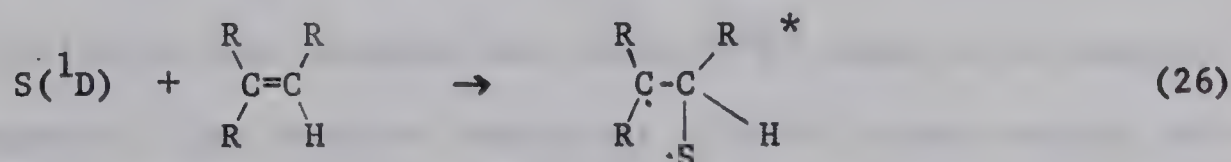


Addition of this step in the steady-state treatment yielded the new expression:

$$\frac{R^O(CO)/2}{R(CO) - R^O(CO)/2} = \frac{k_2 + k_3}{k_2} + \frac{P(O_1)}{P(COS)} \cdot \frac{k_{21} + k_{22}}{k_2} \quad (25)$$

The ratio $(k_{21} + k_{22})/k_2$ was also found to be pressure dependent.

Reaction 21c was proposed to give vinylic mercaptans by the isomerization of a hot intermediate biradical:



Ground state triplet sulfur atoms are found to react, as electrophilic reagents, the rate of addition of $S(^3P)$ atoms to olefins

increases with increasing alkyl substitution on the double bond. Table I compares the results of $S(^3P)$ atoms with those of $O(^3P)$ and $Se(^3P)$.

Unlike $CH_2(^3\Sigma)$ and $O(^3P)$, triplet sulfur atoms add stereospecifically to double bonds, retaining the original configuration of the olefin. With cis and trans-2-butene (26) the episulfide retains the geometrical configuration of the parent olefin (>87 and >98% respectively) not only with singlet, as might be expected, but also with triplet-state sulfur as well.

Objectives and scope of the present investigation

The reactions of sulfur atoms have been observed with C_2 , C_3 and C_4 -olefins and have shown insertion of $S(^1D)$ atoms into C-H bonds and addition of $S(^3P)$ and $S(^1D)$ atoms to double bonds. Random insertion into alkenylic C-H bonds was observed for 1-butene (26) while no insertion into non-terminal vinylic C-H bonds was observed for C_3 and C_4 -olefins. To determine whether this reactivity was general with other olefins the olefin series was extended to include cyclopentene and cyclohexene. Both these members contain two types of alkenylic C-H bonds while having only non-terminal vinylic C-H bonds.

Relative rate studies have shown $S(^3P)$ atoms to be electrophilic reagents. The relative reactivity of $S(^1D)$ atoms towards addition to the double bond, however, has not been established, although it has been found to be less selective in its reactivity than $S(^3P)$ atoms (77). It was felt that information on the relative reactivity of $S(^1D)$ atoms towards addition might be gained by observing relative rates of insertion to addition for a series of substituted olefins. The series of methylated ethylenes was chosen for this study.

Propylene, isobutylene and the 2-butenes have previously been studied and the series was extended to include trimethylethylene and tetramethylethylene.

The effect of halogen atom substitution in olefins and paraffins has also been observed in the present study. The effect of perfluorination on the reactivity of sulfur atoms was observed with perfluorocyclobutene.

Vinyl chloride was chosen to study the effect of an electron withdrawing group on the reactivity of the $S(^3P)$ atom towards the double bond. The electrophilic character exhibited by $S(^3P)$ atoms would predict a decrease in reactivity of vinyl chloride compared to ethylene.

The reaction of $S(^3P)$ atoms with the 2-butenes has resulted in stereospecific addition to the double bond (26). The reaction of $S(^3P)$ atoms with cis and trans-1, 2-dichloroethenes was also studied to determine if this stereospecific addition could be observed with other geometric isomers.

Carbon atoms have been shown to react with C-Cl bonds by an insertion mechanism (112). The possibility of forming sulfenyl chlorides by the insertion of sulfur atoms into C-Cl bonds was investigated. The study included methyl chloride, ethyl chloride and tertiary butyl chloride.

Reactions of divalent species, namely CH_2 , NH and O , with acetylene have not resulted in formation of the corresponding cyclic compounds but only isomerisation products. Reactions of these same species with olefins also resulted in considerable isomerisation and fragmentation. Sulfur atom-olefin reactions, however, do not exhibit similar isomerisations and fragmentations. For this reason it was felt

that reaction of sulfur atoms with acetylene and substituted acetylenes might result in formation of thiacyclopropenes, compounds unknown at present. The COS-alkyne study included acetylene, methyl acetylene, butyne-2 and perfluorobutyne-2.

CHAPTER II

EXPERIMENTAL

The general experimental techniques employed can be divided into two major sections. The first method employed standard high vacuum techniques and apparatus for experiments performed under static conditions. A second experimental technique, flash photolysis-kinetic mass spectrometry, enabled detection of products five milliseconds after the photolytic flash, thus resulting in the identification of short-lived unstable intermediates. A few experiments were also performed using a standard flash photolysis apparatus. This technique was used to obtain spectra of reaction intermediates as well as to study product formation resulting from high intensity photolysis.

STATIC SYSTEM

1) The high-vacuum apparatus

The apparatus (Fig. 1) was a standard pyrex vacuum system evacuated to 10^{-6} torr Hg by means of a two-stage mercury diffusion pump connected to a Welch duoseal Model 1405 mechanical pump. The reaction, storage and analytical sections were kept grease free using Delmar mercury float valves and Hoke helium-tested valves. Absolute gas pressures were measured on a mercury manometer and pressures less than two torr were read on a McLeod gauge. Pressures less than two torr were also monitored in various parts of the system by means of Pirani gauge tubes (Consolidated Electrodynamics Cat. No. GP-001) which were standardised with the McLeod gauge.

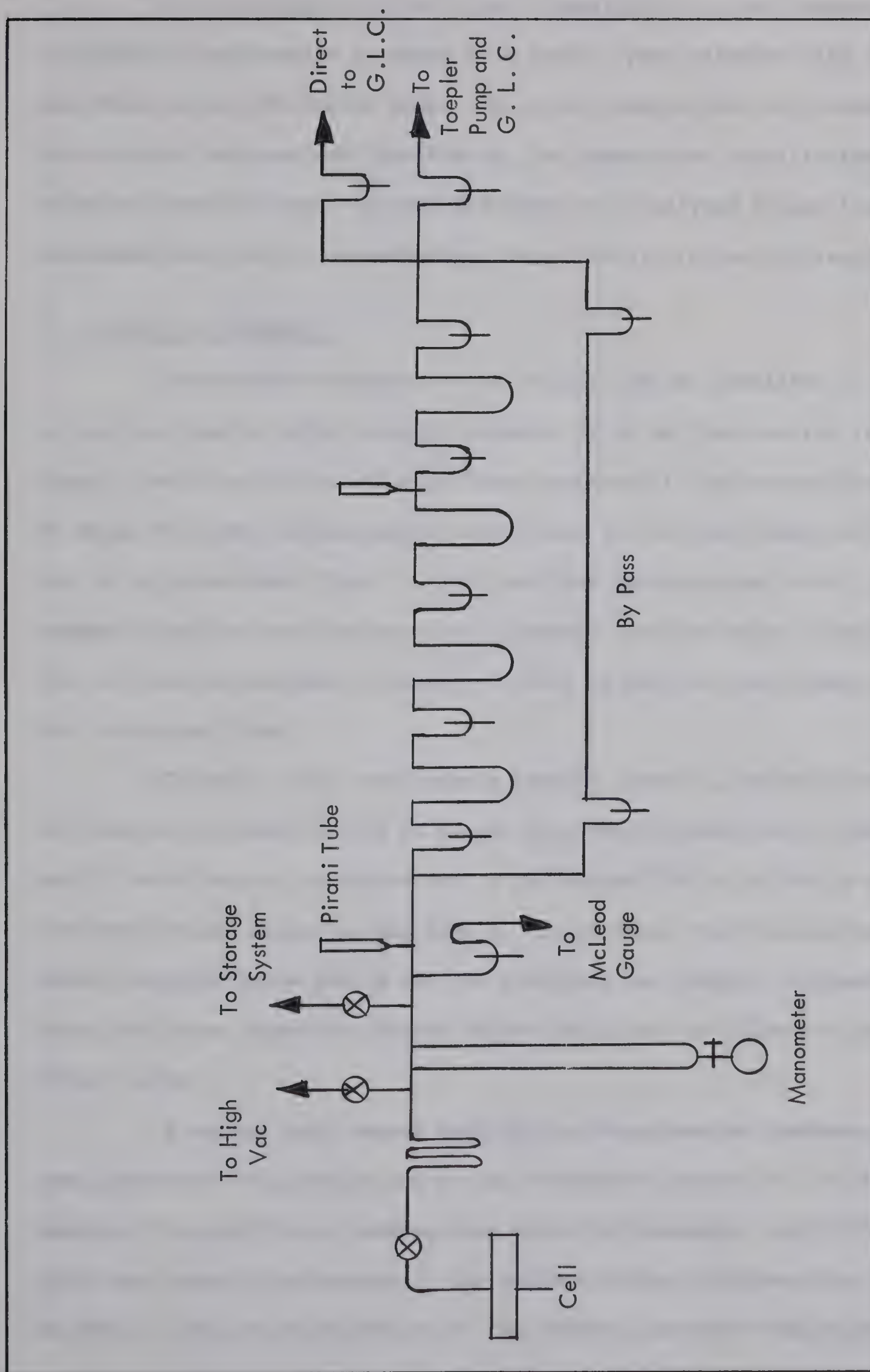


Fig. 1 High Vacuum System

Non-condensable products were transferred to, and measured in, a calibrated gas burette by means of a toepler pump attached with a small one-stage mercury diffusion pump. The total condensibles were separated into product and reactant fractions by low temperature distillations using coil and U-traps. Product fractions were analysed by gas-liquid chromatography (GLC) by transferring them directly to the GLC sampler.

2) Photolytic Assembly

The reaction vessels, in the static system, consisted of cylindrical quartz cells having a diameter of 50 mm. and varying in length from 50 to 200 mm. The cell was connected to the vacuum system by means of a Hoke helium-tested valve which in turn was connected to the cell by a graded seal (Fig. 2). The cell was held in place with a three-pronged clamp and could be kept in a constant position since cleaning of the cell was accomplished by merely filling it with air and flaming it with an oxygen flame.

The main light source was a Hanovia, Type SH, medium pressure arc kept at a distance of 10 to 15 cm. from the incident face of the cell. The effective radiation was in the region 2350 Å to 2500 Å with the most intense region around 2490 Å. Three Vycor 7910 filters removed radiation below 2300 Å and the radiation was roughly collimated using two 50 mm. apertures placed before and after the filters in the filter holder.

A second light source used was an Osram cadmium resonance lamp, connected to a variac and run at a constant current of 1.0 milliamperes. The unfiltered cadmium lamp emits the resonance line 2288 Å which very nearly corresponds to the maximum of the COS absorption at 2235 Å. The intensity output of the cadmium lamp was found to be

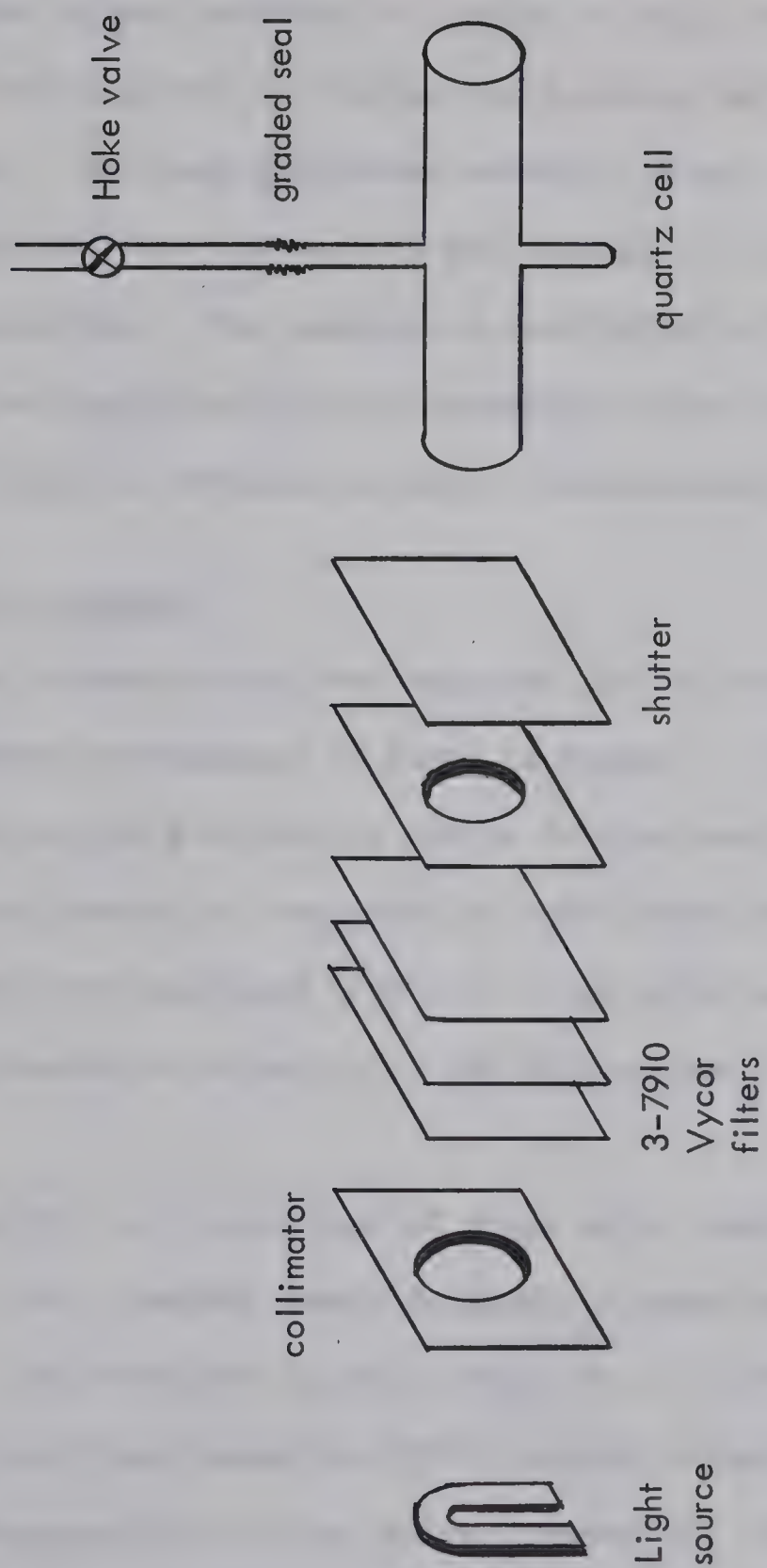


Fig. 2 Photolysis apparatus

reproducible to ca. 3% although the total absorbed intensity was a factor of 2 or 3 less than the medium pressure mercury arc.

When it was necessary to obtain a large amount of product (for N.M.R. analysis etc.) a coiled low pressure mercury resonance lamp was used. The lamp was placed around a 50 mm. by 200 mm. cell made of Vycor 7910 and the mercury was removed to eliminate any Hg-sensitised reactions. The absorption coefficient of COS at 2537 Å is very low but owing to the high intensity of the coil lamp large conversions could be obtained in only a few minutes of irradiation.

3) Analytical Assembly

Gas chromatography was employed for all quantitative analyses. The experimental arrangement is shown in Figure 3. Non-condensibles were measured in the gas burette and no further analysis was necessary as, in the COS system, it consisted of only carbon monoxide. Condensable fractions were analysed by GLC by first being measured in the gas burette or transferred directly to the GLC sampler from the distillation train.

The GLC unit consisted of three major components; a thermal conductivity cell (Gow-Mac Model TR IIIB), a power supply (Gow-Mac Model 999-C) and a Sargent recorder (Cat. No. S-72180). The thermal conductivity cell was heated to 175° F; higher temperatures were avoided to prevent decomposition of the sulfur compounds. The detector current was kept constant at 250 milliamperes.

A single stream He flow was used as carrier gas. The helium was dried by passing it through a molecular sieve 13X column immersed in liquid nitrogen. The molecular sieve was reactivated periodically

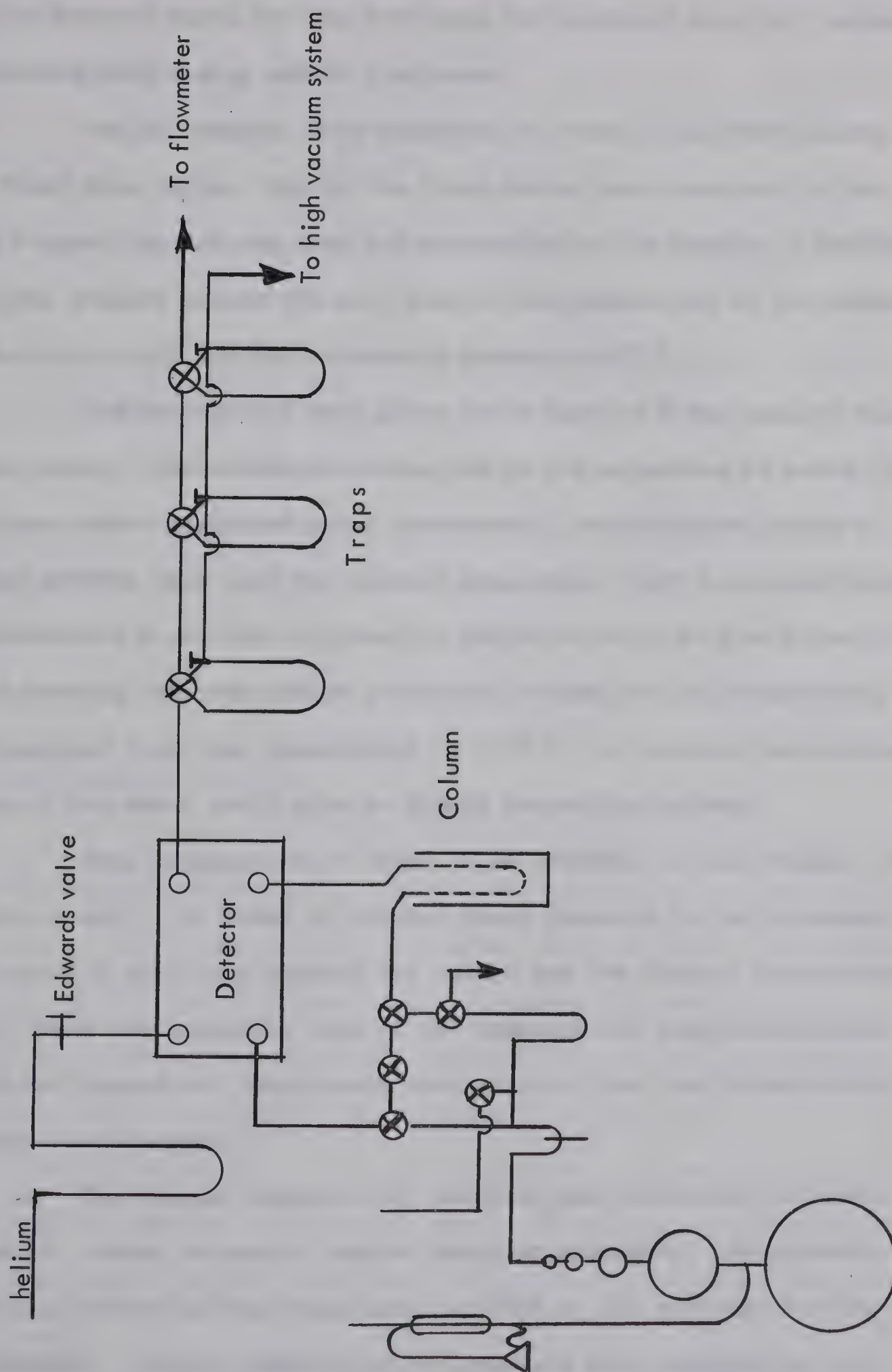


Fig. 3 Analytical Apparatus

by heating to 200° C with a heating tape. The gas flow was controlled with an Edwards valve and the flow rate was measured on an oil manometer calibrated with a soap bubble flow meter.

The GLC sampler unit consisted of three 3-way Hoke valves and one 2-way Hoke valve. One of the 3-way valves was connected to the high vacuum line and was used for evacuation of the sampler. Heating tape was wrapped around the exit side of the sampler up to the thermal conductivity cell and was constantly heated to 50° C.

The GLC columns were glass coils made of 6 mm. outside diameter glass tubing. The column was connected to the apparatus by means of silicone rubber seals and metal connectors. Two different types of column packing were used for product separation: 10% o-tricresylphosphate on Chromosorb W and 18% silicone oil 550-2% stearic acid on Kromat. A metal heating tube was placed around the column and the temperature could be regulated from room temperature to 150° C. If cooling was required a dewar of ice water could also be placed around the column.

Some compounds were found to be unstable in the thermal conductivity cell. In order to collect these products it was necessary to install a cold trap between the column and the thermal conductivity cell. Once the retention time of the compound had been established, it could be trapped out immediately upon elution from the column before it reached the detector.

The thermal conductivity detector was calibrated for each compound. Where authentic samples were not available, the products from the photolysis reactions were purified by GLC and used for the calibration. Several samples of the compound were measured in the gas burette and transferred to the GLC sampler. The calibration of a

compound was always made in the same detector region as found experimentally for product yields. Chromatographic peak areas were measured with an Ott planimeter and in all cases a linear detector response was observed with increasing amount of sample. With samples having vapor pressures greater than 20 torr Hg calibrations were reproducible to ca. 5%. For compounds having low vapor pressures at room temperature calibrations were obtained using a gas burette supplied with a water jacket through which hot water, at a regulated temperature, could be passed. In cases where more than one isomer, of a high molecular weight sulfur compound, was produced, the GLC was calibrated for the most volatile compound and the detector response was assumed to be the same for the other isomers. This assumption was found to be quite valid since the variations in detector response for different isomers were found to be within the experimental limits of the calibration.

4) Experimental Procedure

Substrate pressures were measured with a mercury manometer and the reactants were distilled into the cell through a coil trap immersed in a low temperature slush bath. This procedure was necessary to keep the cell mercury free thus eliminating photosensitisation reactions. Mercury was initially removed from the cell by immersing the coil trap, next to the cell, in liquid nitrogen for 15 minutes while heating the cell to 75° C with a heat gun. By monitoring the transmitted resonance line 2537 Å, from a low pressure mercury arc, with a photocell, it was found that the mercury could be removed in a few minutes.

The reactants were allowed to equilibrate for 1 hour prior to irradiation and the lamp was also given a 1 hour warm-up period.

TABLE II
G.L.C. OPERATING CONDITIONS AND ELUTION TIMES FOR
SULFUR COMPOUNDS

Compound	Column ^a	Column Temperature (°C)	Elution Time (mins.)
cyclopentene episulfide	I	70	7.5
cyclopentene-3-thiol	I	70	4.5
cyclopentene-4-thiol	I	70	4.5
cyclopentene-1-thiol	I	70	14.0
cyclohexene episulfide	I	40	14.0
cyclohexene-3-thiol	I	40	6.0
cyclohexene-4-thiol	I	40	6.0
trimethylethylene	V	50	11.5
trimethylethylene mercaptan -1 ^b	V	50	10.0
-2	V	50	16.5
-3	V	50	18.5
tetramethylethylene episulfide	IV	46	4.5
tetramethylethylene mercaptan	IV	46	10.0
vinyl chloride episulfide	III	60	22.5
2-chlorovinyl mercaptan	III	60	19.0
<u>trans</u> -1, 2-dichloroethylene episulfide	I	47	3.0
<u>cis</u> -1, 2-dichloroethylene episulfide	I	47	15.0

TABLE II
(continued)

Compound	Column ^a	Column Temperature (°C)	Elution Time (mins.)
carbon disulfide	III	75	4.5
benzene	III	75	10.5
thiophene	III	75	12.5
perfluorotetramethylthiophene	II	50	7.5
tertiary butyl chloride mercaptan	I	35	5.5
ethylene episulfide	II	50	2.0
2-chloroethyl mercaptan	II	50	20.0

a. Column I = 10% o-tricresylphosphate on chromosorb W;
0.5 ft. length, 1 mm ID

Column II = 10% o-tricresylphosphate on chromosorb W;
4 ft. length, 4 mm ID

Column III = 10% o-tricresylphosphate on chromosorb W;
8 ft. length, 4 mm ID

Column IV = 18% silicone oil 550, 2% stearic acid on
Kromat C; 2 ft. 4 mm ID

Column V = 18% silicone 550, 2% stearic acid on
Kromat C; 8 ft. 4 mm ID

b. Three mercaptans (1, 2 and 3) were produced in the reaction with trimethylethylene but their exact structures were not determined.

c. The carrier gas flow rate in each case was 65 cc/min. helium.

Nearly complete self-reversal of the 2537 Å line was observed for the medium pressure mercury lamp after 1 hour operation.

After irradiation, the contents of the cell were frozen in the cold finger with liquid nitrogen. The non-condensibles were removed with the aid of the one stage mercury diffusion pump and the Toepler pump; two additional U-traps between the cell and the gas burette were kept at -196°C to prevent loss of any condensibles. The contents of the cell were warmed-up and re-frozen twice to free any non-condensibles trapped in the solid matrix. The reactants were distilled off at various temperatures using appropriate low temperature slush baths and the remaining heavier sulfur products were transferred directly to the G.L.C. sampler for gas chromatographic analysis.

Individual products were trapped in the G.L.C. trapping train, degassed and transferred under vacuum to break seals, N.M.R. tubes etc. for further analysis.

Mass spectra were obtained on a Metropolitan-Vickers Model MS2 spectrometer operating at 70 eV.

Infrared spectra were obtained on a Perkin Elmer Infracord using a micro gas cell of path length 7.5 cm.

N.M.R. spectra were obtained on a Varian 100 Mc spectrometer. All samples were dissolved in carbon tetrachloride; a trace of tetramethylsilane was added as a standard.

Due to the instability of many of the sulfur compounds, samples were always kept in liquid nitrogen or refrigerated until just before running the spectra.

TABLE III
MATERIALS USED

Material	Source	Grade and Purity	Purification
Cyclopentene	A.P.I.	A.P.I. Certified	None
Cyclohexene	Eastman Organic	Reagent	Distilled from chloro-benzene slush (-45°)
Trimethyl-ethylene	Matheson, Coleman and Bell	Reagent	Distilled from dry ice-acetone slush (-78°)
Tetramethyl-ethylene	Chemical Procurement Laboratories	Reagent	Distilled from chloro-form slush (-64°)
Vinyl chloride	Matheson	C.P. Grade (99%)	Distilled from ethanol slush (-115°)
<u>Cis</u> -1, 2-dichloro-ethylene	Eastman Organic	Technical (95%)	g.c. 20 ft. silicone rubber column
<u>Trans</u> -1, 2-dichloro-ethylene	Eastman Organic	Technical (95%)	g.c. 20 ft. silicone rubber column
Acetylene	Matheson	Contained acetone	Distilled several times from ethyl chloride slush (-139°)
Methyl acetylene	Matheson	Technical (97%)	Distilled from ethanol slush (-115)
Dimethyl acetylene	Farchan Research Laboratories	Reagent (99%)	Distilled from dry ice-acetone slush (-78°)

TABLE III
(continued)

Material	Source	Grade and Purity	Purification
Perfluorocyclo- butene	Peninsular	Technical (98%)	Distilled from n- heptane slush (-91°)
Perfluoro- butyne-2	Columbia Organic Chemicals	C.P. Grade (99%)	Distilled from ethanol slush (-115°)
Carbon Dioxide	Airco	High Purity	None
Helium	Canadian Helium Co.	Technical	Passed through molec- ular sieve trap at -195
Teriary-butyl chloride	Eastman Organic	Technical (97%)	G.c. 20 ft. silicone rubber column
Methyl chloride	Matheson	99%	Distilled from 1- chlorobutane slush (-123°)
Ethyl chloride	Matheson	U.S.P. Grade 99.7%	Distilled from n- heptane (-91°)
Ethylene episulfide	Prepared		Distilled from methanol slush (-98°) and de- gassed at n-heptane (-91°)
Propylene episulfide	Prepared		Distilled from dry ice-acetone slush (-78°) and degassed at n-pentane (-131°)

TABLE III
(continued)

Material	Source	Grade and Purity	Purification
Propylene	Phillips	Research	None
Chlorodi- fluoro- methane	Matheson	High purity (99.9%)	Distilled from n- pentane (-131)
Hydrogen sulfide	Matheson	C.P. Grade (99.5%)	None
KSCN	Nichols	Reagent	None
Ethylene carbonate	Eastman Organic	Reagent	None
Propylene carbonate	Eastman Organic	Reagent	None
Carbonyl sulfide	Matheson	Contains H ₂ S	H ₂ S removed by passing through saturated NaOH solution. Gas dried and distilled from n-pentane (-131°) and de- gassed from iso- pentane (-160°)

FLASH PHOTOLYSIS WITH KINETIC MASS SPECTROMETRY

1. Apparatus

An Atlas CH₄ mass spectrometer equipped with an Atlas EW246 electron multiplier was used in this study. The original inlet system was removed from the instrument and replaced by a specially-designed assembly of a Vycor 7910 tube sealed to a small metal leak on the ion chamber to which a 4" -bore CVC oil diffusion pump was attached. The Vycor tube, surrounded by a spiral shaped quartz flash discharge lamp, served as the photolysis cell. A schematic illustration of the assembly is given in Fig. 4.

The power source of the flash lamp was a 12 kv, 20 μ F low inductance capacitor with a suitable power supply. The signal from the mass spectrometer was fed into an Analab dual trace oscilloscope, Type 1120, and photographed with a polaroid camera. The flash of the lamp triggered the oscilloscope through a photocell.

The response time of the instrument was 4-5 milliseconds, making possible the detection and quantitative measurements of intermediates with half-lives of this order of magnitude. The mass spectrometer was tuned in each measurement at the correct m/e value of the species to be measured.

2. Procedure

Premixed, ultra-pure COS (400×10^{-3} torr), the substrate under investigation (800×10^{-3} torr) and Airco reagent grade helium (14 torr), was passed into the photolysis cell, flashed, and the flashed mixtures analysed for each detectable transient consecutively by the mass spectrometer.

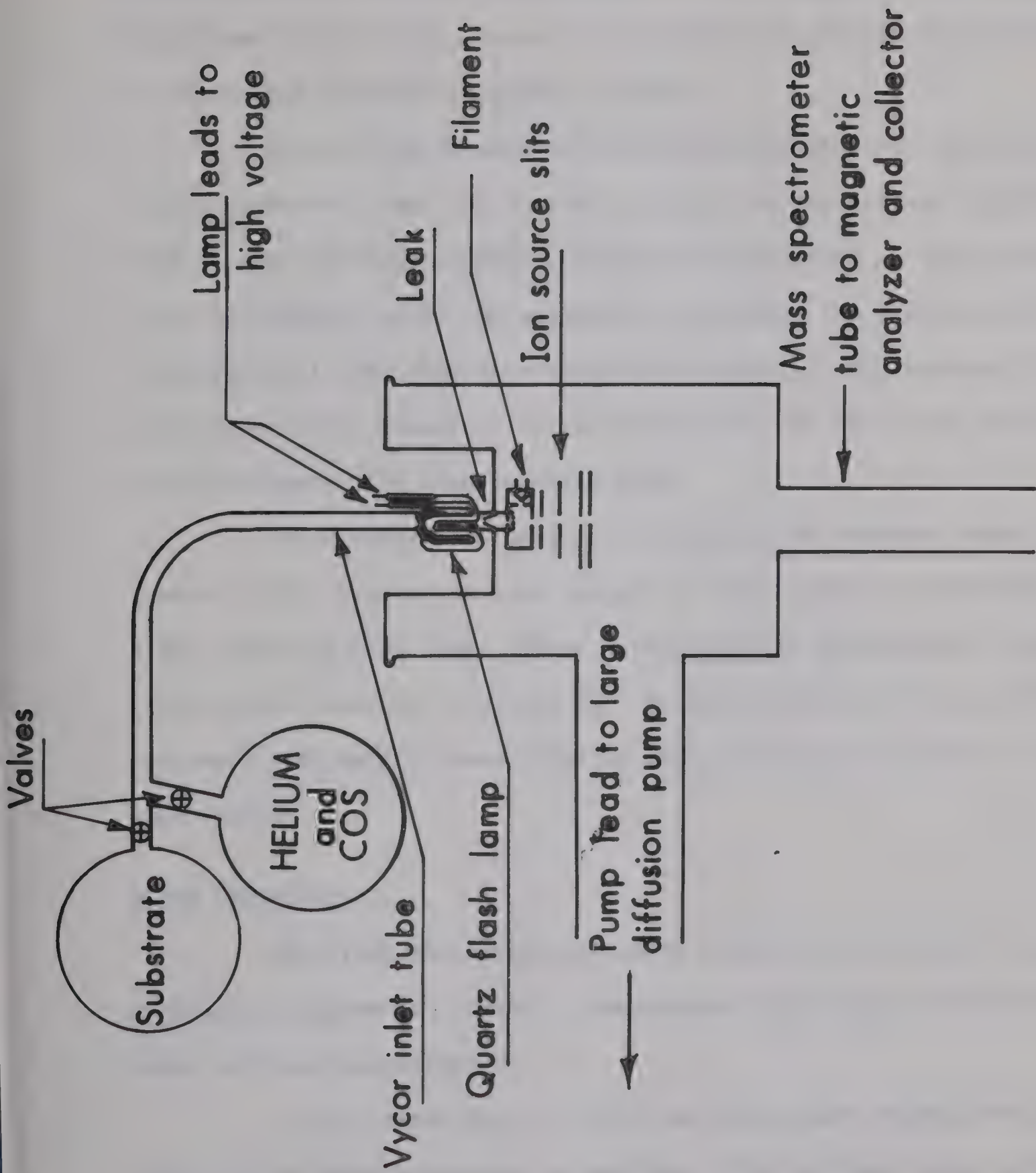


Fig. 4 Flash photolysis-kinetic mass spectrometry apparatus.

Before each series of flashes the system was flashed with only helium in the cell and blank checks were obtained for the particular m/e values in question. In all cases background signals were found to be negligible compared to product signals.

Decay of the signal with time was observed even for known stable products. This was due to a decrease in the product concentration in the ionisation chamber caused by the bleedout of the products from the reaction cell. To meaningfully evaluate the time-resolved oscillograms it was therefore necessary to correct for the drop in signal due to the normal bleedout. After correction, the corrected oscillogram represented the true reaction path.

Corrections were made by multiplying the observed signal for a known stable product by such factors as would make the corrected signal constant with time. These multiplication factors were found to give results accurate to within 5%. Periodic checks of the bleedout rate were made during these investigations and were found not to change appreciably.

FLASH PHOTOLYSIS

The flash photolysis apparatus consisted of standard flash photolysis components; namely, a photolysis flash lamp, spectroscopic lamp, cell and spectrograph.

A $41\mu\text{F}$ capacitor, at 9 kV, was discharged through two 55 cm. quartz flash lamps connected in parallel. The two lamps were joined near the ends. The photolysis lamp was filled with 7 torr N_2 and 80 torr krypton while the spectroscopic lamp contained 100 torr krypton. The $3\mu\text{F}$ capacitor for the spectroscopic flash was usually charged to

10 kV. Transient ultraviolet absorption spectra were recorded on Kodak 103 a-0 plates exposed in a Hilger medium quartz spectrograph.

The reaction vessel was a cylindrical cell 50 cm. long and 4.3 cm. in diameter and was constructed of Vycor 7910 (transmitted wavelength $> 2200 \text{ \AA}$). The cell had plane parallel quartz windows. A helium tested Hoke-valve connected the cell to a standard vacuum rack facilitating filling of the cell and removal of the products. Products of the reaction were analysed by G.L.C. techniques previously described.

CHAPTER III

A. THE REACTIONS OF SULFUR ATOMS WITH:

1. Cyclopentene.

Results.

2. Cyclohexene.

Results.

3. Perfluorocyclobutene.

Results.

4. Trimethylethylene.

Results.

5. Tetramethylethylene.

Results.

B. DISCUSSION.

RESULTS

1. Cyclopentene

When carbonyl sulfide was photolysed with cyclopentene, in low conversion runs, four products were found. According to their mass spectra, shown in Appendix A, all four were isomeric addition products with the molecular weight of 100, i.e., C_5H_8S . Gas chromatographic analysis of the condensable reaction products, however, showed only three separable peaks with the following retention times 1.00 (I): 1.75 (II) : 3.20 (III) on a 0.5 ft. T.C.P. column. The N.M.R. spectrum of peak I (Figure 5) showed two products to be present in the ratio 2:1. It showed two sets of doublets in the SH region at τ values of 8.36, 8.42 and 8.55, 8.58 and two singlets in the vinylic proton region at τ values of 4.28 and 4.34. Since the SH hydrogen atoms of vinylic mercaptans exhibit resonance in the region of τ values of 7.3 to 7.8 (74), these two compounds were identified as the two alkenyl mercaptans cyclopentene-3-thiol and cyclopentene-4-thiol. By analogy with the COS-cyclohexene system (vide infra), where statistical insertion into the 3 and 4 positions was observed, the cyclopentene-3-thiol is tentatively assigned as the larger product while cyclopentene-4-thiol is formed in the smaller yield.

The largest product, compound II, was identified by its mass spectrum and N.M.R. spectrum to be the cyclopentene episulfide. This was also confirmed by the fact that it is the only product formed from the reaction of $S(^3P)$ atoms with cyclopentene. Triplet

N.M.R. SPECTRA

Mixture of cyclopentene-3-thiol and cyclopentene-4-thiol

ASSIGNMENTS (τ)

cyclopentene-3-thiol

c. 4.28

d. 8.55 and 8.58

cyclopentene-4-thiol

a. 4.34

b. 8.36 and 8.42

Ratio of cyclopentene-3-thiol/cyclopentene-4-thiol is ca.2

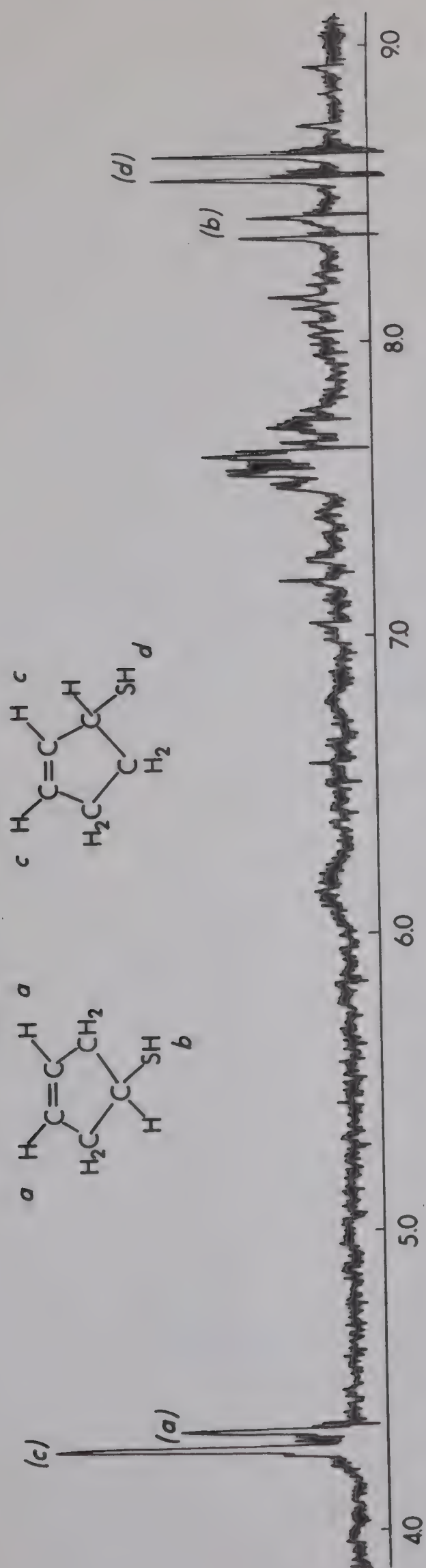


Fig. 5 Nuclear Magnetic Resonance Spectra of a mixture of cyclopentene-3-thiol and cyclopentene-4-thiol.

N.M.R. SPECTRA

Cyclopentene Episulfide; C_5H_8S

ASSIGNMENTS (τ)

a. 6.83

b. 7.8 to 8.6

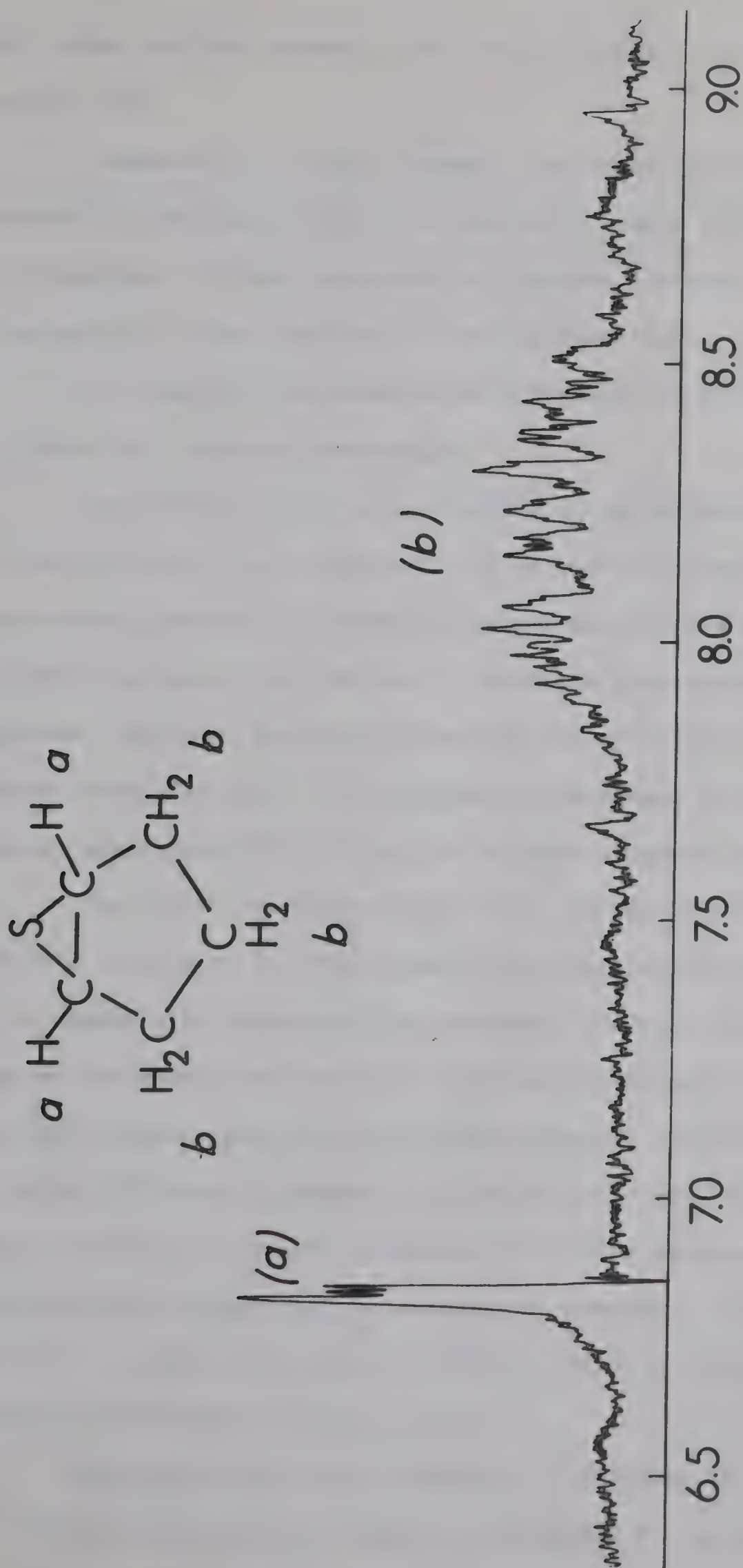


Fig. 6 Nuclear Magnetic Resonance Spectrum of Cyclopentene Episulfide.

sulfur atoms have been shown to react with olefins to give only the episulfide (71).

Compound III, a minor product, was identified as the vinylic mercaptan cyclopentene-1-thiol. An authentic sample of this product was synthesised (75) and its retention time was identical with that of compound III, using the same column and conditions.

The reaction was examined as a function of substrate pressure, added CO_2 , time and wavelength.

The product rates, as a function of cyclopentene pressure, are shown in Table IV and Figure 7. It is seen that the products increase with increasing substrate pressure and reach a maximum value at pressures greater than 200 torr. The ratio $R(\text{mercaptan})/R(\text{episulfide})$ is pressure dependent reaching a limiting maximum value of 0.80 at pressures about 200 torr. $R(\text{CO})$ gradually decreases with olefin pressure, approaching $R^0(\text{CO})/2$ at the highest pressure used (300 torr).

The effect of the inert gas, CO_2 , on the reaction is shown in Table V and Figure 8. The isomeric distribution of products is seen to change with increasing CO_2 pressure, the rate of mercaptan formation decreasing and the rate of episulfide formation increasing. Thus, while without CO_2 , the ratio $R(\text{mercaptan})/R(\text{episulfide})$ is 0.44, with 1250 torr CO_2 present, the above ratio has a value of 0.03. A slight increase in product formation and slight decrease in CO production was observed with increasing CO_2 pressure. The total yield of the products (in terms of $R^0(\text{CO}) - R(\text{CO})$), however, was found to be independent of CO_2 pressure.

The reaction was also studied as a function of exposure time. The data are shown in Table VI and Figure 9. At larger

TABLE IV
VARIATION IN PRODUCT YIELDS WITH CYCLOPENTENE PRESSURE
IN THE COS-CYCLOPENTENE SYSTEM^a

Rates, μ moles/30 min.

P(cyclo- C ₅ H ₈) torr	CO	CO ^O -CO	RSH(3+4) ^b	RSH(1) ^c	E.S.	Total C ₅ H ₈ S	$\frac{\text{RSH}}{\text{ES}}$	% Recovery ^d
0	10.7	10.7	0	0	0	0	--	--
0	10.6	10.6	0	0	0	0	--	--
25.2	6.92	3.68	0.45	0	1.70	2.15	0.27	59
51.0	6.41	4.19	0.85	0	1.92	2.77	0.44	66
103.3	6.03	4.57	1.05	0.03	2.00	3.08	0.54	67
151.1	5.93	4.67	1.12	0.06	1.90	3.08	0.62	66
204.1	5.83	4.77	1.54	0.10	2.04	3.68	0.81	77
251.1	5.64	4.96	1.44	0.12	2.12	3.68	0.74	74
306.6	5.60	5.00	1.40	0.16	1.96	3.52	0.80	71

a. P(COS) = 100 torr; Exposure time = 30 min.

b. cyclopentene-3-thiol + cyclopentene-4-thiol

c. cyclopentene-1-thiol

d. In terms of R^O(CO) - R(CO)

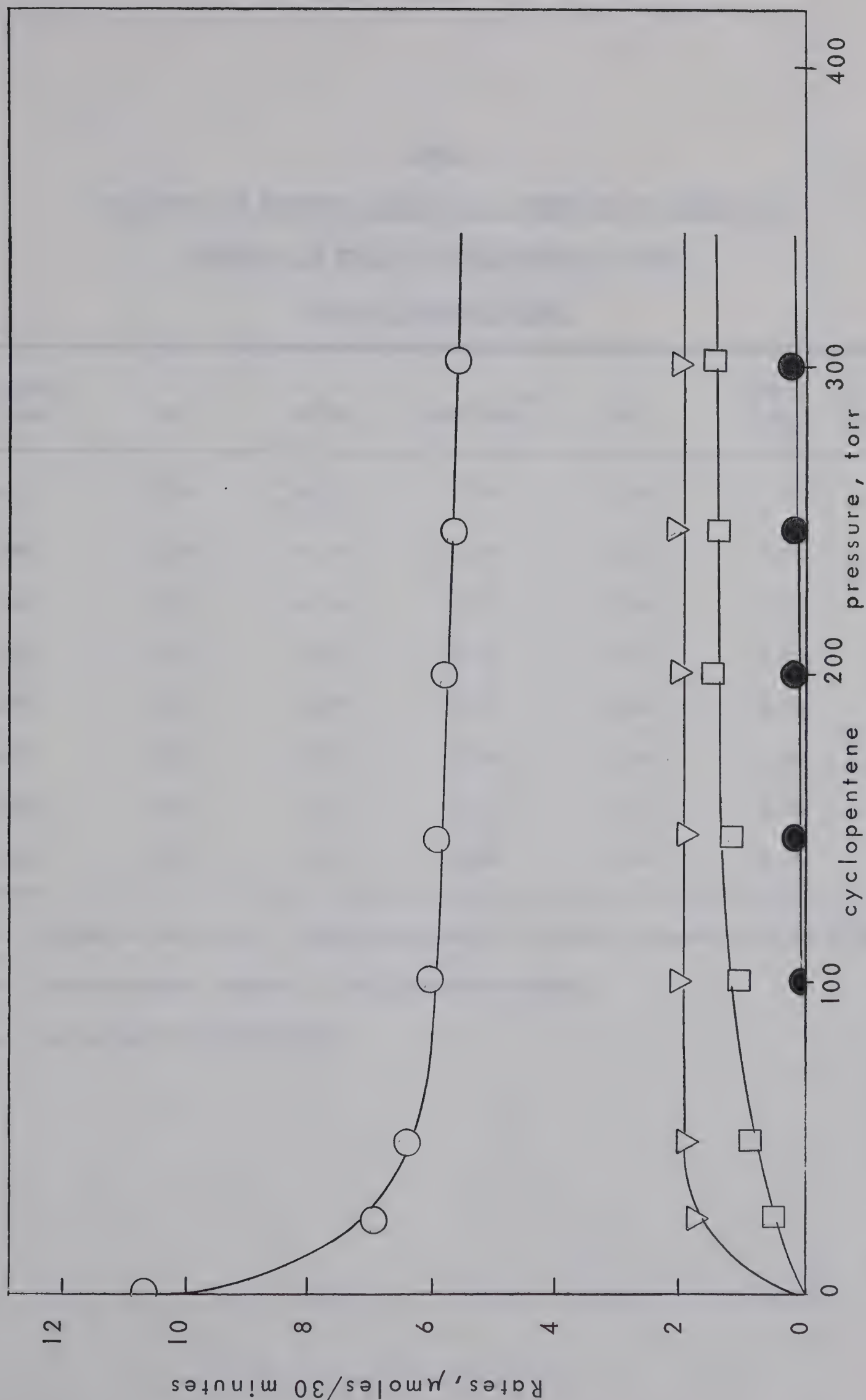


Fig. 7 Variation in product yield with cyclopentene pressure.

○ = CO; ▽ = cyclopentene episulfide; □ = cyclopentene-3-thiol +
 ● = cyclopentene-1-thiol

TABLE V
VARIATION IN PRODUCT YIELDS AS A FUNCTION OF ADDED CO₂
PRESSURE IN THE COS-CYCLOPENTENE SYSTEM^a

Rates, μ moles/30 min.

P(CO ₂) torr	CO	CO-CO ^o	RSH(3+4) ^b	ES	Total C ₅ H ₈ S	% Recovery ^c
0	6.41	4.19	0.85	1.92	2.77	66
100	5.90	4.70	0.64	2.32	2.96	63
216	5.90	4.70	0.63	2.62	3.25	69
422	5.56	5.04	0.30	2.36	2.66	53
620	5.51	5.09	0.33	3.01	3.34	66
839	5.53	5.07	0.24	3.16	3.40	67
1039	5.45	5.15	0.21	3.25	3.46	67
1249	5.37	5.23	0.08	3.18	3.26	62

a. P(COS) = 100 torr; P(cyclopentene) = 51 torr; Exposure time = 30 min.

b. cyclopentene-3-thiol + cyclopentene-4-thiol

c. In terms of R(CO)-R(CO)

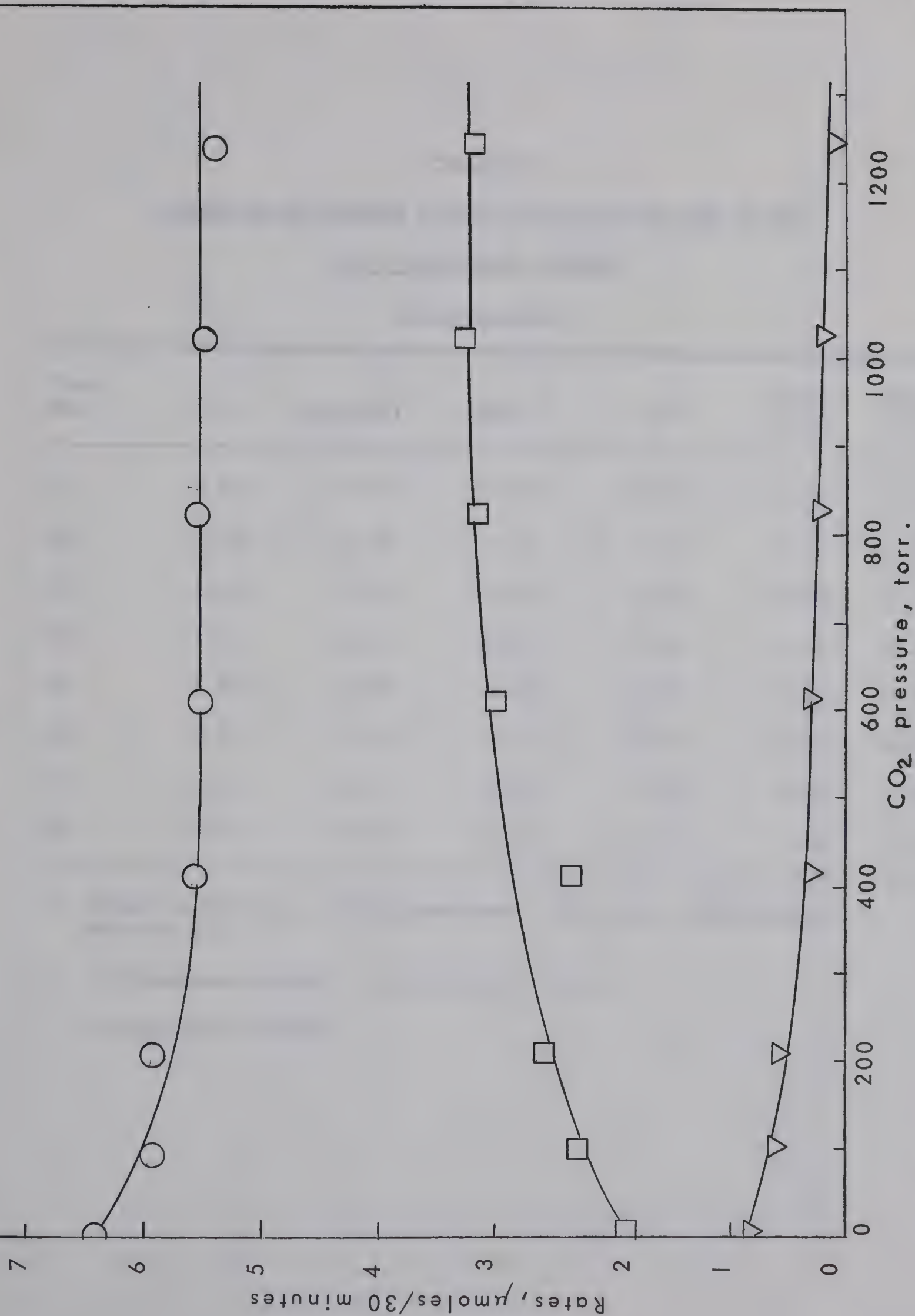


Fig. 8 Variation in product yields as a function of added CO₂ pressure.

○ = CO; □ = cyclopentene-3-thiol + cyclopentene-4-thiol; ▽ = cyclopentene-4-thiol

TABLE VI
VARIATION IN PRODUCT YIELDS WITH REACTION TIME IN THE
COS-CYCLOPENTENE SYSTEM^a

Yields, μ moles

Time Min.	CO	RSH(3+4) ^b	RSH(1) ^c	ES	Total C ₅ H ₈ S	Ratio RSH/ES
15	2.42	0.52	0.04	0.77	1.32	0.73
30	4.38	1.16	0.06	1.65	2.87	0.74
30	4.38	1.04	0.06	1.57	2.67	0.70
45	7.02	1.72	0.13	2.44	4.31	0.76
60	8.66	2.30	0.19	3.40	5.89	0.73
60	9.46	1.98	0.13	3.40	5.51	0.62
75	10.33	2.59	0.20	4.07	6.86	0.69
90	12.30	3.00	0.26	4.65	7.91	0.70

a. P(COS) = 100 torr; P(cyclopentene) = 247 torr; Medium press.
Mercury Arc.

b. cyclopentene-3-thiol + cyclopentene-4-thiol

c. cyclopentene-1-thiol

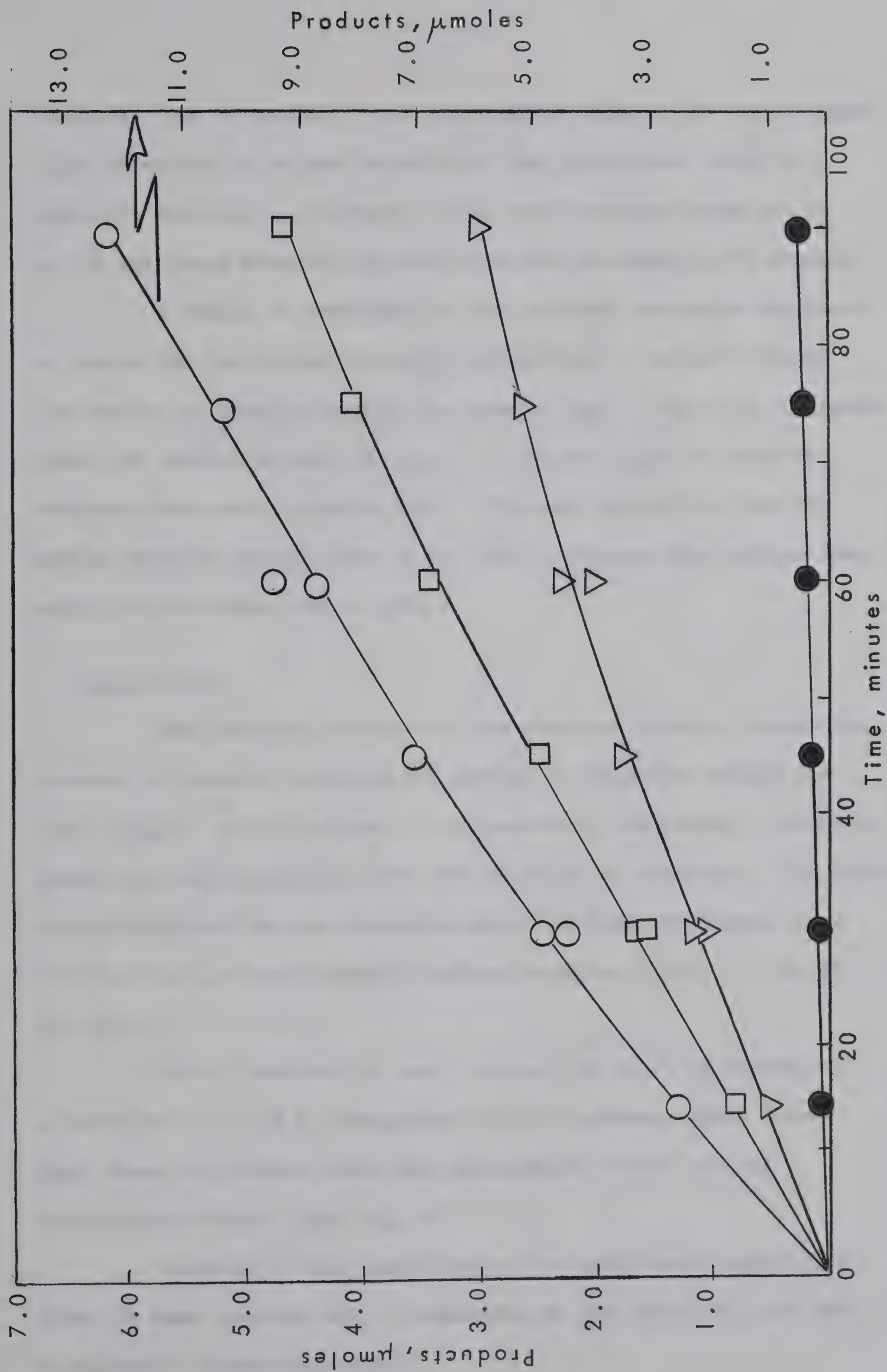


Fig. 9 Variation in product yields with reaction time
 \bigcirc = CO; \square = cyclopentene episulfide; ∇ = cyclopentene-3-thiol + cyclopentene-4-thiol

exposures, due to secondary reactions and attenuation of the incident light intensity by polymer deposition, the yields were found to gradually decrease. A decrease in the total product formation of ca. 8% was found when the exposure time was increased to 90 minutes.

A change in wavelength of the incident radiation was found to change the ratio $R(\text{mercaptan})/R(\text{episulfide})$. Table VII shows the results of photolysis with the cadmium lamp. This ratio increased from 0.80 (medium pressure Hg arc) to 0.92 when light of shorter wavelength was used (cadmium lamp). The main absorption from the medium pressure mercury lamp is ca. 2490 Å, whereas the cadmium lamp emits its resonance line at 2288 Å.

2. Cyclohexene

Mass spectral analysis of the reaction products showed the presence of isomeric products all having the molecular weight 114 i.e., $C_6H_{10}S$. As in the case of cyclopentene, two isomeric products showed the same retention times and could not be separated. The total products yielded two gas chromatographically separable peaks, on a 0.5 ft. T.C.P. column, having relative retention times of 1.00 (I) : 2.1 (II).

N.M.R. analysis of peak I showed two products present in a ratio of 1:1. N.M.R. assignments of the resonance peaks showed that these two products were the cyclohexene-3-thiol and the cyclohexene-4-thiol (See Fig. 10).

Compound II was identified as the cyclohexene episulfide from its mass spectrum and by comparison of its retention time with an authentic commercial sample.

TABLE VII
VARIATION IN PRODUCT YIELDS WITH REACTION TIME
IN THE COS-CYCLOPENTENE SYSTEM^a

yield, μ moles

Time Min.	CO	RSH(3+4) ^b	RSH(1) ^c	ES	Total C ₅ H ₈ S	Ratio RSH/ES
15	2.14	0.38	0.02	0.45	0.85	0.89
30	4.25	0.76	0.02	0.90	1.68	0.89
45	6.35	1.29	0.04	1.40	2.73	0.95
75	10.02	2.46	0.13	2.65	5.24	0.97

a. P(COS) = 100 torr; P(cyclopentene) = 250 torr; Cadmium lamp.

b. cyclopentene-3-thiol + cyclopentene-4-thiol

c. cyclopentene-1-thiol

N.M.R. SPECTRA

Mixture of cyclohexene-3-thiol and cyclohexene-4-thiol.

ASSIGNMENTS (τ)

cyclohexene-3-thiol

a. 4.34

b. 8.62 and 8.67

cyclohexene-4-thiol

c. 4.40

d. 8.54 and 8.59

Ratio of cyclohexene-3-thiol/cyclohexene-4-thiol ca. 1.

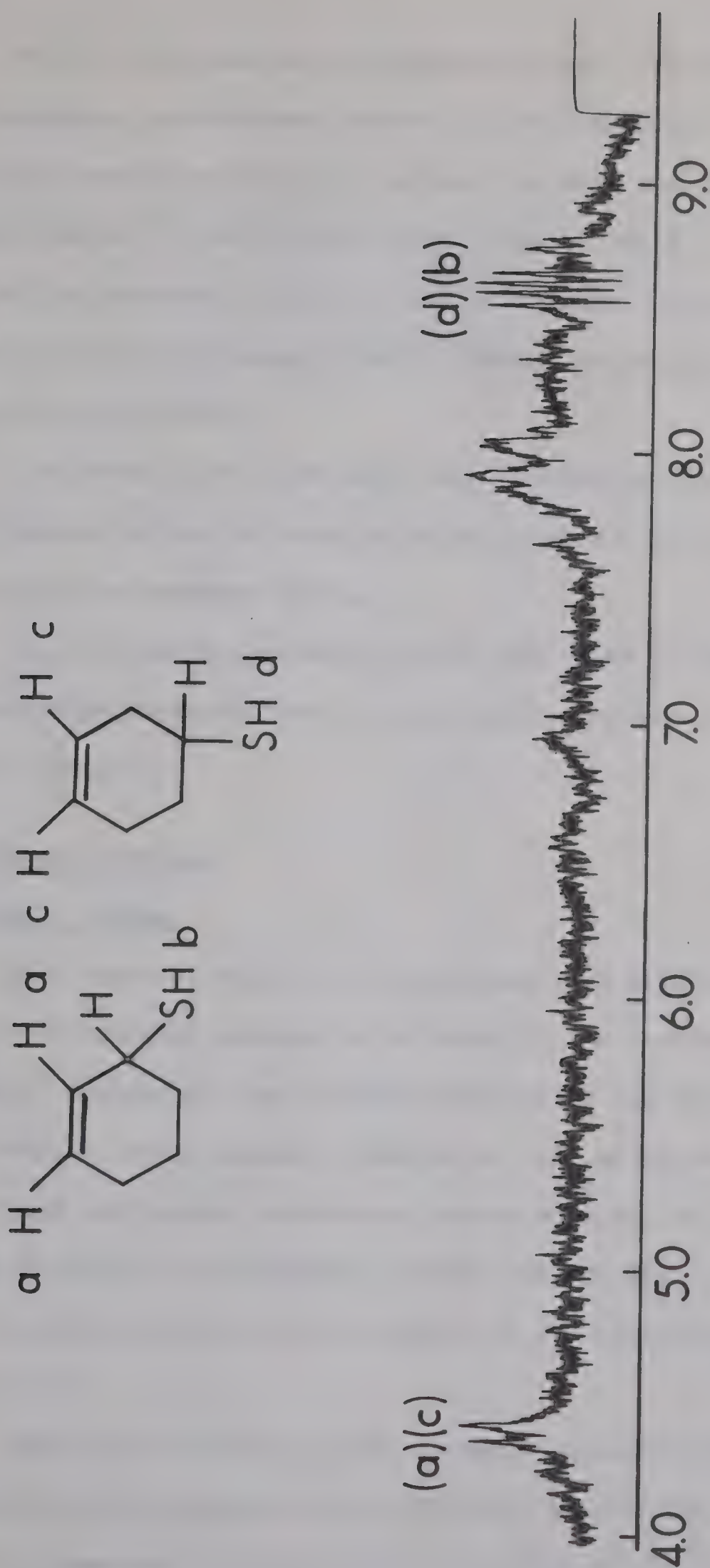


Fig. 10 Nuclear Magnetic Resonance Spectrum of a mixture of cyclohexene-3-thiol and cyclohexene-4-thiol.

Unlike cyclopentene, cyclohexene did not yield any of the vinylic mercaptan, cyclohexene-1-thiol, in low conversion runs. During large conversion photolysis a fourth product was formed in very small yields. It was found to elute last on the g.c. column just as did cyclopentene-1-thiol in the cyclopentene system. It is therefore probably cyclohexene-1-thiol although no analysis could be made on this trace product.

A mixture of COS (100 torr) and cyclohexene (76 torr) yielded products in the ratio mercaptan/episulfide = 0.81 as compared to 0.50 in the cyclopentene system.

In this system the inert gas CO_2 was found to completely suppress mercaptan formation with a simultaneous increase in the episulfide formation.

3. Perfluorocyclobutene

A. Static system

When carbonyl sulfide was photolysed with perfluorocyclobutene no volatile condensible products were formed in the reaction. The only product, besides CO, was a solid deposited on the walls of the reaction vessel. Upon complete oxidation of this solid the gaseous products found were sulfur dioxide and carbon dioxide; the SO_2 comprising 95 mole % of the gaseous product and the CO_2 only ca. 5%. This would indicate that the major product of the reaction must be elemental sulfur.

The rate of carbon monoxide formation decreased slowly with increasing substrate pressure and at pressures greater than 1000 torr the CO value appeared to be approaching the value $R^0(\text{CO})/2$ (Table VIII and Figure 11).

TABLE VIII

VARIATION IN PRODUCT YIELDS WITH PERFLUOROCYCLOBUTENE PRESSURE
IN THE COS-PERFLUOROCYCLOBUTENE SYSTEM^a

Rates, μ moles/30 min.

P(cyclo-C ₄ F ₆) torr	CO	Condensible Product
0	7.68	--
26.0	6.67	0
49.0	6.48	0
74.1	6.63	0
153.3	6.54	0
154.1	6.43	0
203.9	5.82	0
286.2	4.87	0
450.6	4.67	0
716.5	4.28	0
1017.0	4.21	0

a. P(COS) = 100 torr; exposure time = 30 min.

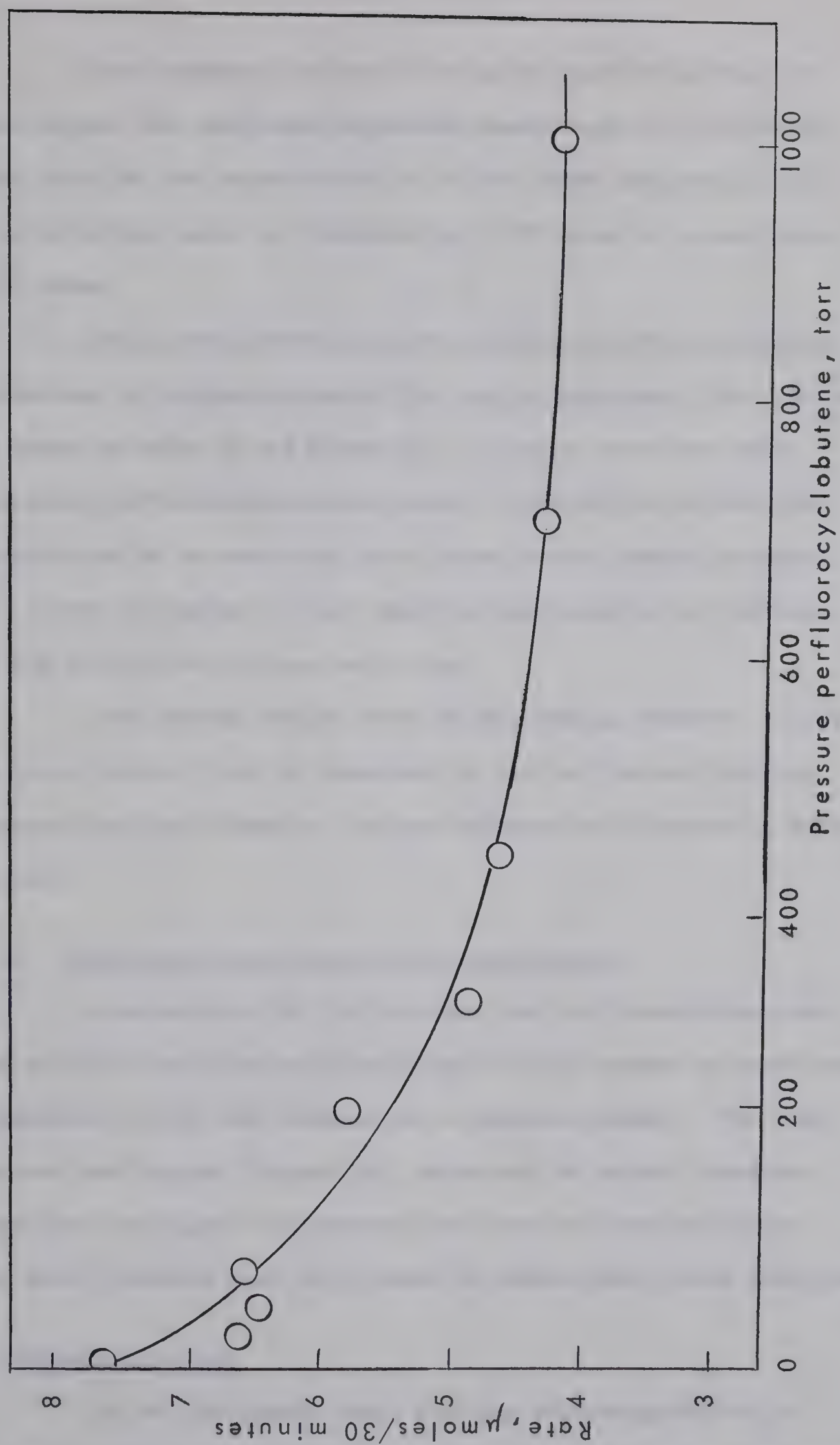


Fig. 11 CO formation as a function of perfluorocyclobutene pressure.

$\bigcirc = \text{CO}$.

With elemental sulfur as the major reaction product it would appear that perfluorocyclobutene reacts only as an efficient third body for the recombination of sulfur atoms and possibly also as an efficient agent for deactivating $S(^1D)$ atoms to ground state $S(^3P)$ atoms.

This latter possibility was checked by adding perfluorocyclobutene to a known system of COS and cyclopentene. The results are shown in Table IX and Figure 12. It can be seen that with increasing perfluorocyclobutene pressure the yield of episulfide increases while the mercaptan yield shows a simultaneous decrease. This effect is similar to that observed upon addition of the inert gas CO_2 to the COS-cyclopentene system.

This system differs from the CO_2 system, however, in that the total product yield is dependent on the perfluorocyclobutene pressure; the yield showing a slight decrease with increasing substrate pressure.

B. Flash photolysis-kinetic mass spectrometry

A mixture of COS (400 microns) and perfluorocyclobutene (800 microns) was flash photolysed and a sulfur adduct of perfluorocyclobutene, C_4F_6S , was observed as a reaction product. The time-resolved oscillogram (Figure 14), corrected for normal bleed-out, shows that the signal is permanent and shows no decay with time. This would indicate that the product is stable under these conditions.

4. Trimethylethylene

In low conversion runs, four gas chromatographically-separable sulfur containing compounds were formed with the following

TABLE IX
VARIATION IN PRODUCT YIELDS AS A FUNCTION OF ADDED PERFLUORO-
CYCLOBUTENE IN THE COS-CYCLOPENTENE SYSTEM^a

Rates, μ moles/30 min.

P(cyclo- -C ₄ F ₆) torr	CO	CO ^o -CO	RSH(3+4) ^b	ES	Total C ₅ H ₈ S	% Recovery ^c
0	4.62	3.06	0.84	1.55	2.39	78
0	4.64	3.04	0.84	1.45	2.29	75
51.6	4.57	3.11	0.56	1.50	2.06	67
205.2	4.00	3.68	0.44	1.73	2.17	59
505.0	3.74	3.94	0.31	1.92	2.23	57

a. P(COS) = 100 torr; P(cyclopentene) = 75.1 torr; exposure time = 30 min.

b. cyclopentene-3-thiol + cyclopentene-4-thiol

c. In terms of R^o(CO)-R(CO)

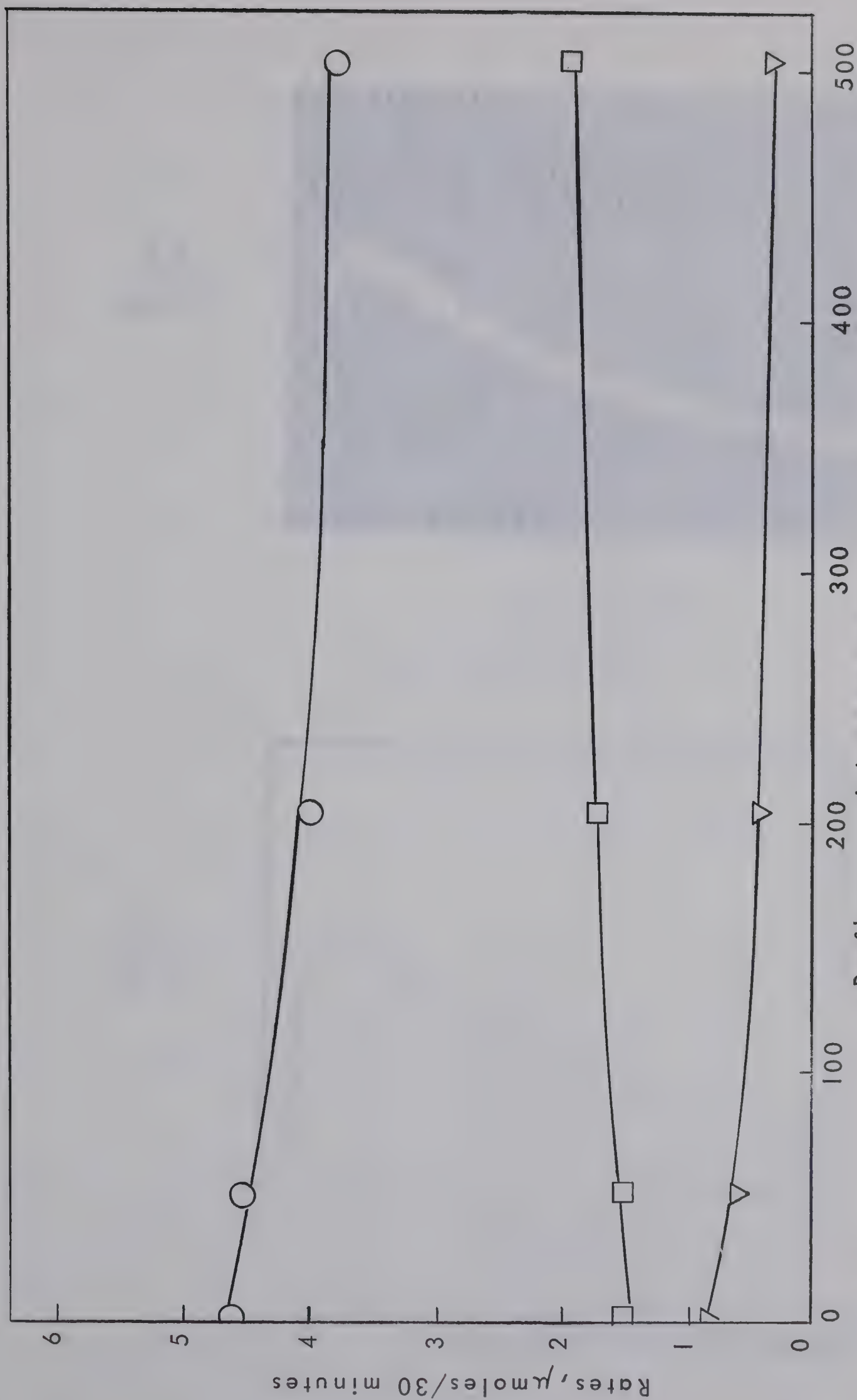
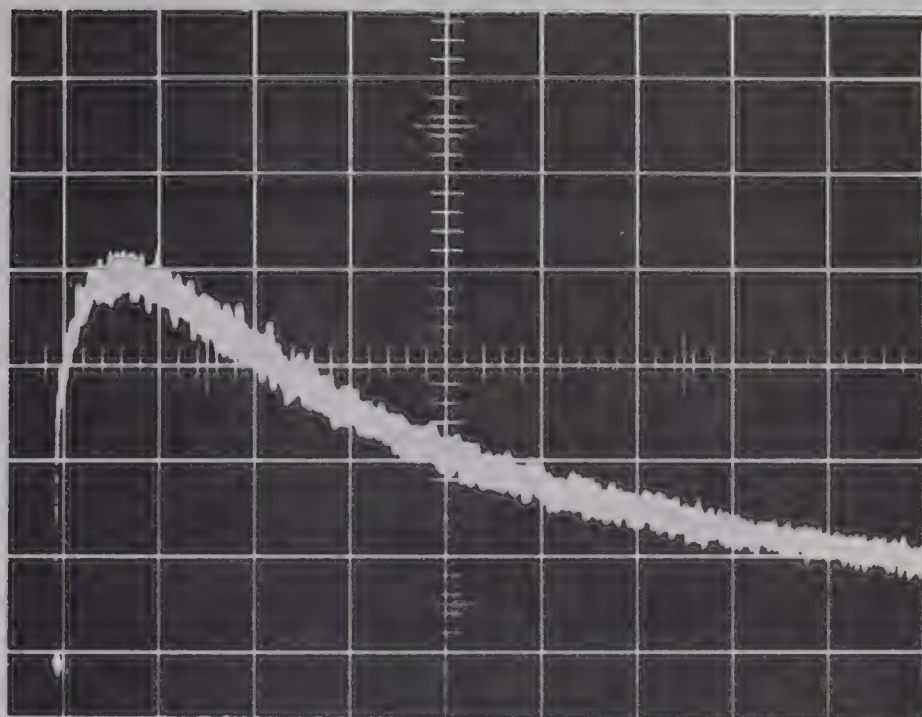


Fig. 12 Variation in product yields as a function of added perfluorocyclobutene in the COS-cyclopentene system. \bigcirc = CO; \square = cyclopentene-3-thiol + cyclopentene-4-thiol; ∇ = cyclopentene episulfide

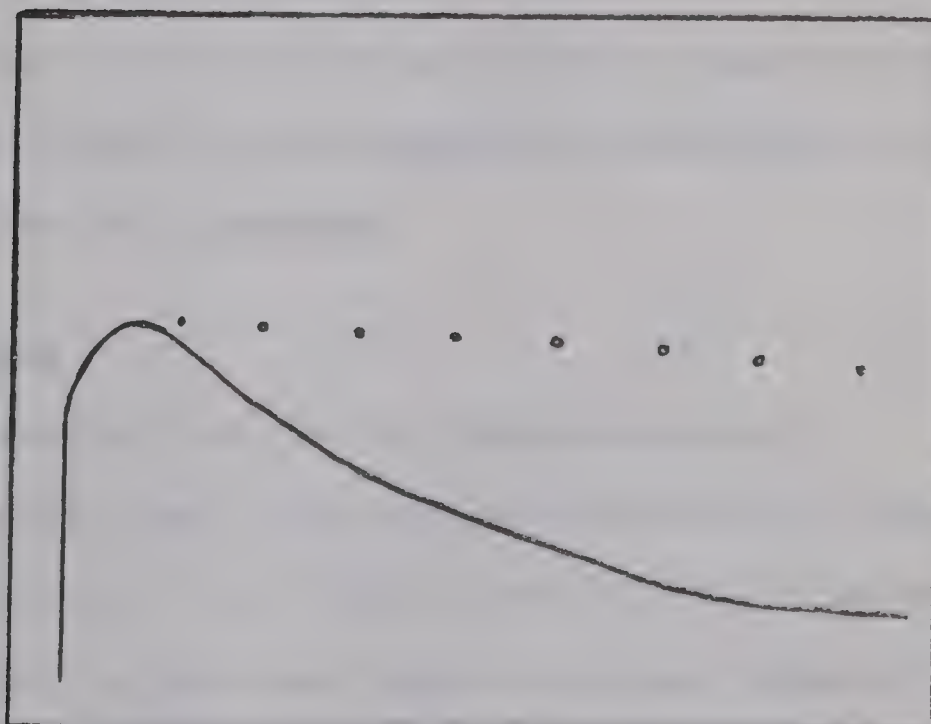
50.0
Millivolts
per div.



0.5 seconds per div.

Fig. 13 Mass 194, \hat{C}_4F_6S

50.0
Millivolts
per div.



0.5 seconds per div.

Fig. 14 Mass 194, \hat{C}_4F_6S
Dotted line corrected for bleed-out.

relative retention times 1.00 (I) : 1.11 (II) : 1.62 (III) : 1.83 (IV), on an 8 ft. 18% silicone oil 550, 2% stearic acid column. From their mass spectra, given in Appendix A, all four were isomeric addition products with molecular weights of 102, i.e. $C_5H_{10}S$.

Upon addition of CO_2 to this system only compound II was formed, the other three products being completely suppressed. Carbon dioxide has been shown to be efficient in deactivating $S(^1D)$ atoms to $S(^3P)$ atoms. Furthermore from previous work (71) it is known that $S(^3P)$ atoms react with olefins producing only the episulfide. Thus compound II must be the trimethylethylene episulfide, with the other three products being isomeric mercaptans. Individual identification of the three mercaptans was not made. However, all three likely arise from insertion into the C-H bonds of the three different methyl groups of the substrate molecule.

In a mixture of 100 torr COS and 300 torr trimethylethylene the product ratio was found to be $R(\text{mercaptan})/R(\text{episulfide}) = 0.73$ (mercaptan = 42% of the total products).

5. Tetramethylethylene

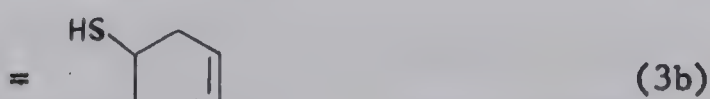
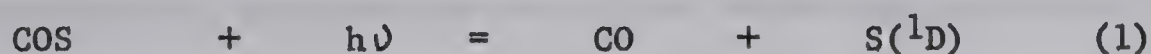
In low conversion runs, two gas chromatographically separable compounds were found. They had relative retention times of 1.00 (I) : 2.16 (II) on a 2 ft. 18% silicone oil 550, 2% stearic acid column. According to their mass spectra both were isomeric addition products with molecular weights of 116, i.e. $C_6H_{12}S$. Identification of the episulfide was made in a manner identical to that used for trimethylethylene. Addition of CO_2 increased the yield of episulfide and decreased the yield of the mercaptan.

In a mixture of 100 torr COS and 125 torr tetramethylethylene the product ratio $R(\text{mercaptan})/R(\text{episulfide})$ was 0.73 (mercaptan = 42% of the total products). This ratio is probably somewhat lower than the maximum value that would be obtained in a higher pressure region. It has been observed for other olefins that the ratio $R(\text{mercaptan})/R(\text{episulfide})$ increases with substrate pressure until a ratio of O_1/COS of 3 or greater has been obtained. This ratio would therefore probably be ca. 1 (mercaptan = ca. 50%) in the high pressure region.

Addition of 1200 torr CO_2 to this mixture reduced this ratio to 0.11.

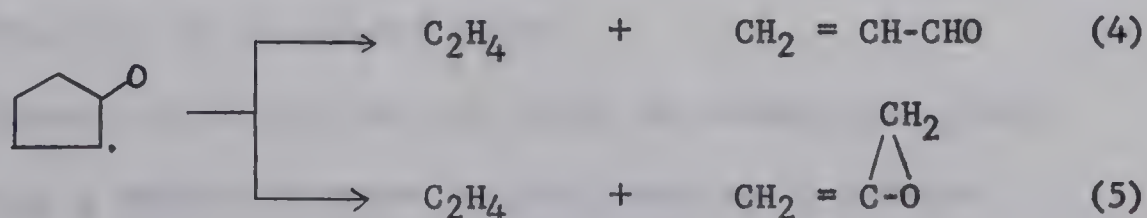
DISCUSSION

The primary products formed in the COS-cyclopentene system are CO, cyclopentene episulfide, cyclopentene-1-thiol, cyclopentene-3-thiol, and cyclopentene-4-thiol. To a first approximation the primary reactions are:



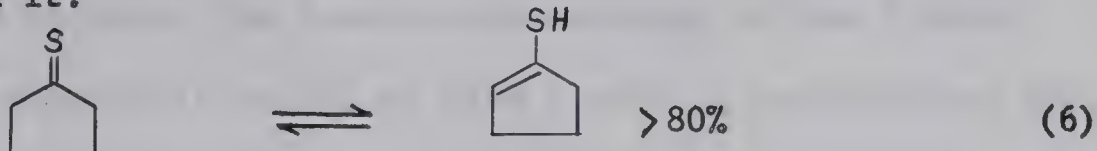
The alkenyl mercaptans, cyclopentene-3-thiol and cyclopentene-4-thiol, account for ca. 40% of the total product yield. From the butenes, where the number of alkylic C-H bonds per C=C bond is about the same (5-6 : 1), the alkenyl mercaptan yield was ca. 30% (26). The ratio of these mercaptans was 2:1 and although it was not possible to obtain definite analytical isomeric assignments, it is probably safe to assume, by analogy to the COS-1-butene system (26) and the COS-cyclohexene system, that they arise from statistical insertion at the 3- and 4- positions. Small yields of the vinylic mercaptan, cyclopentene-1-thiol, up to ca. 5% of the total, were also detected. The tautomeric equilibrium between the 1-thiol and the thioketone has been shown to proceed spontaneously at room temperature and is strongly shifted to the thiol side (75).

Product recoveries varied with experimental conditions, and the optimum values were ca. 75% in the high pressure regions. The loss was probably due to some polymerisation process, although the possibility of cracking reactions cannot be excluded. In the reaction of $O(^3P)$ atoms with cyclopentene one of the major products is ethylene (27%) formed in a pressure-independent fragmentation (53). The mechanism of this reaction has not been investigated in detail. The appearance of olefins among the cracking products in the O-atom reactions is not common and it may indicate a molecular rather than free radical mode of decomposition. One possibility for the molecular split would be:



The exothermicity resulting from addition of $S(^1D)$ and $O(^3P)$ atoms is nearly equal; if any of the analogous reactions occur in the S-atom system all the products escaped detection.

The apparent low yield of cyclopentene-1-thiol may be due to some characteristic of the reaction producing it, or perhaps this product is lost due to trimerisation of the thioketone in tautomeric equilibrium with it.



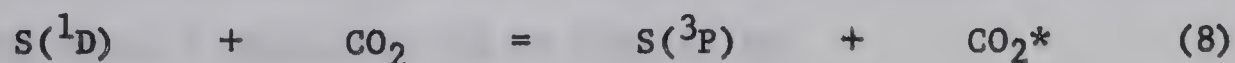
The trimerisation of thiocyclopentanone is catalysed by strong acids such as HCl but in the pure liquid state this compound has been shown to trimerise only very slowly, unlike open chain thioketones and thioaldehydes which are known to trimerise immediately.

This low yield of vinylic mercaptan, however, is consistent with the results observed with cis and trans-2-butenes where only trace quantities of vinylic mercaptans were formed (26). Only ethylene and propylene have been shown to produce appreciable quantities of vinylic mercaptans, their yields being ca. 50% and 15% respectively (71), and in the case of propylene only the terminal mercaptan was produced. This would indicate that production of vinylic (at least non-terminal vinylic) and alkenylic mercaptans does not occur from competitive $S(^1D)$ atom insertion reactions but from two distinctly different mechanisms. This will be discussed later.

The product distribution was found to change with wavelength upon using a medium pressure mercury lamp and a cadmium

resonance lamp. Photolysis with the medium pressure mercury lamp resulted in a ratio $R(M)/R(E) = 0.80$ while with the cadmium resonance lamp $R(M)/R(E) = 0.92$. The main absorption by COS from the mercury lamp is ca. 2490 Å, corresponding to an energy of 114.8 kcal./Einstein, while the energy of the 2288 Å cadmium resonance line is 124.0 kcal./Einstein. Although the exact excess energy distribution between the S atom and CO is unknown, the translational energy of the S atom produced by the photolysis of COS at 2288 Å will be greater than that of the S atom produced by photolysis at 2490 Å. An estimated maximum difference in translational energies of the two sulfur atoms, based on equipartition of energy, is ca. 5 kcal./mole. With decreasing wavelength, therefore, the rate of insertion, relative to the rate of addition to the double bond, increases. A similar increase in the rate of insertion of translationally hot $S(^1D)$ atoms was observed in the reactions of sulfur atoms with paraffins (73).

The effect of CO_2 on the reaction (Figure 9) is explained in terms of an efficient electronic relaxation of the excited $S(^1D)$ atoms to the ground state:



It has been shown that mercaptans arise solely from $S(^1D)$ atom precursors, whereas episulfides are formed from $S(^3P)$ and $S(^1D)$ atoms. If we take the relative yield of mercaptan as a measure of the $S(^1D)$ atom concentration in the system, at 1250 torr of added CO_2 more than 90% of the $S(^1D)$ atoms are quenched. The CO yield is also slightly retarded by CO_2 . From previous work it is known that the rate constant ratio $k(S + \text{olefin})/k(S + COS)$ is at least 30 times

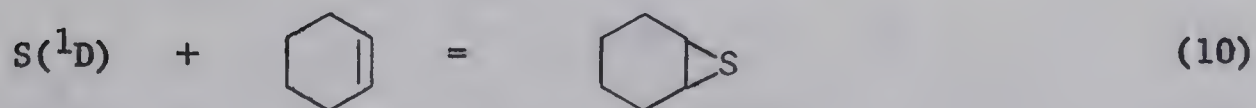
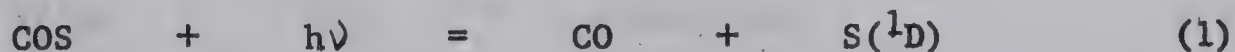
larger for triplet than for singlet S-atoms (67). Consequently conversion of $S(^1D)$ to $S(^3P)$ will diminish the significance of the abstraction step



with a concomittant decrease in $R(CO)$ to the limit of $R^0(CO)/2$. But this would require that at high CO_2 pressures $R(\text{episulfide})/R(CO) = 1$, while experimentally it is only 0.67.

Secondary photolysis of products has also been shown to be partly responsible for reducing the yield of the sulfur-containing products from the theoretical 100% (as calculated from the $R(CO)$ decrease). Figure 9 shows that when the irradiation time is increased to 90 minutes the rate of production of products decreases by ca. 8%. This together with polymerisation, cracking of hot products and loss due to mechanical handling of the high molecular weight sulfur products could account for the optimum yield of 75% obtained in these reactions.

The primary products formed in the COS-cyclohexene system are CO, cyclohexene episulfide, cyclohexene-3-thiol and cyclohexene-4-thiol. The overall reactions can be written as:

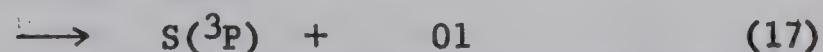
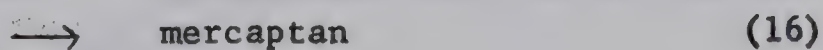
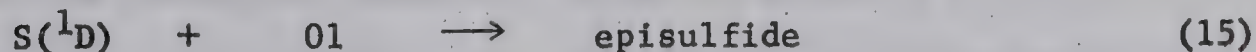
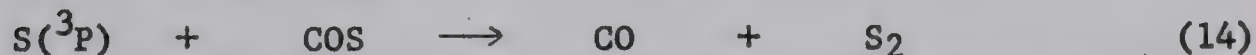


At long exposures a fourth product was found having the same relative retention time as the cyclopentene-1-thiol in the cyclopentene system. This additional product may well be the vinylic mercaptan, cyclohexene-1-thiol.

Under identical conditions it was observed that the ratio $R(M)/R(E)$ was somewhat larger for cyclohexene than for cyclopentene. This increase could be explained by the larger number of CH_2 groups in cyclohexene.

The insertion products cyclohexene-3-thiol and cyclohexene-4-thiol were obtained in the ratio 1:1, indicating random insertion into the C-H bonds of the substrate molecule. The species undergoing insertion is $S(^1D)$ since high pressures of CO_2 suppress the mercaptan formation with a simultaneous increase in cyclohexene episulfide.

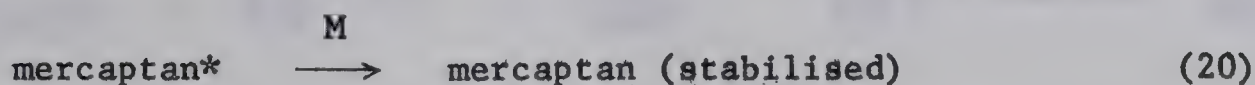
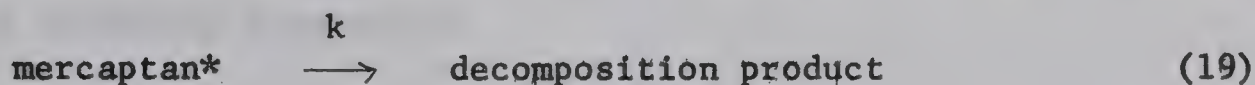
The mechanism for the reaction of sulfur atoms with olefins must include the following steps:



The competition for sulfur atoms by the olefin in steps 15, 16, 17 and 18 accounts for the CO decrease with increasing substrate pressure.

The CO yield reaches a limiting value of $R^0\text{CO}/2$, where $R^0(\text{CO})$ is the CO formation in the absence of olefin, corresponding to complete scavenging of the initially produced sulfur atoms.

Table IV shows a pressure dependence on the ratio $R(\text{M})/R(\text{ES})$, its value being 0.27 at low olefin pressure and increasing to a constant value of 0.80 at high pressures. This effect may be partly due to inefficient stabilization of the hot mercaptan, at low pressures, resulting in decomposition as indicated by the lower yield in this pressure region. Assuming that the low mercaptan/episulfide ratio, in the low pressure region, is due to decomposition of the mercaptan, a minimum life-time for the hot mercaptan can be estimated.



Assuming that deactivation of the excited molecule occurs on every collision, the rate constant for decomposition is given by:

$$k = \frac{(\text{decomposition product})}{(\text{mercaptan})} \cdot z \quad (21)$$

where z is the collision frequency. From the pressure data in Table IV, k is ca. $6 \times 10^8 \text{ sec.}^{-1}$. The minimum life-time of the hot mercaptan is therefore ca. $1.7 \times 10^{-9} \text{ sec.}$

A second possible contribution, is the deactivation of $\text{S}(^1\text{D})$ atoms by COS, resulting in an additional source of $\text{S}(^3\text{P})$ atoms which give rise only to episulfide formation. At low pressures a competition for the $\text{S}(^1\text{D})$ atom exists between the olefin and COS. COS can

efficiently deactivate the $S(^1D)$ atom to $S(^3P)$ (70) and reaction 18 is much faster than reaction 14, as shown in recent mercury-photosensitized reactions (79), therefore resulting in additional episulfide formation. At high olefin pressures reaction 13 is eliminated and a constant ratio $R(M)/R(ES)$ is obtained.

Reaction 17, deactivation of $S(^1D)$ atoms by the olefin, probably also occurs by analogy with that found for paraffins (73). The importance of this reaction, however, cannot be quantitatively measured.

If the slow abstraction from COS by $S(^3P)$, reaction 14, is set equal to zero, steady-state treatment of the proposed mechanism yields the following expression:

$$\frac{R^O(CO)/2}{R(CO) - R^O(CO)/2} = \frac{k_{12} + k_{13}}{k_{12}} + \frac{(O1)}{(COS)} \cdot \frac{k_{15} + k_{16} + k_{17}}{k_{12}} \quad (22)$$

A plot of the L.H.S. of the equation vs. $(O1)/(COS)$ for the cyclopentene system is shown in Figure 15. The data appear to fit a straight line at low $(O1)/(COS)$ ratios but at high pressures of olefin the data show a large deviation from linearity.

$R(CO)$, in the high olefin pressure region, approaches the value $R^O(CO)/2$, thus $R(CO) - R^O(CO)/2$ is the small difference between two numbers and the deviation from linearity is probably due to experimental error.

A closer examination of the low pressure region indicates that the data will fit a small but definite curvature. If the slopes are calculated from equation 22, the rate constant ratio $(k_{15} + k_{16} + k_{17})/k_{12}$ decreases to a minimum and then rises again. To simplify

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$$\frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} \right) = \frac{1}{2}$$

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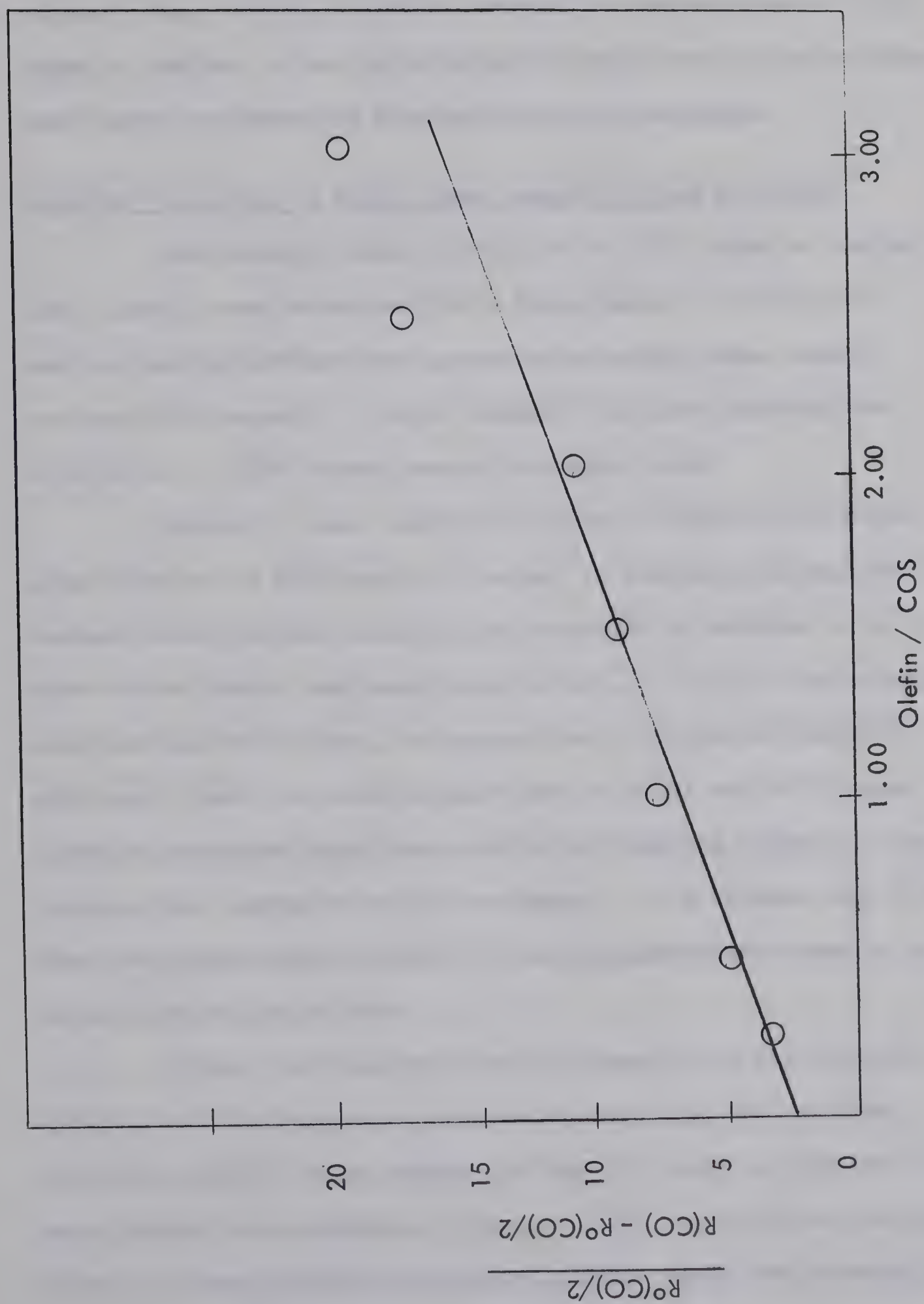


Fig. 15 $\frac{R^{\circ}(CO)/2}{R(CO) - R^{\circ}(CO)/2}$ vs. $Olefin / COS$
For the COS-cyclopentene system.

the kinetic expression, the CO producing reaction, reaction 14, was eliminated from the mechanism during the steady-state treatment. Although the reaction is slow as compared to the addition of $S(^3P)$ atoms to olefins, it may be appreciably significant in the low pressure region and cannot be eliminated from the mechanism.

Relative reactivity of $S(^1D)$ atoms towards C-H and C=C bonds.

The relative rates of addition of $S(^3P)$ atoms to olefins have recently been determined for a large number of olefins (77) and the results indicate that ground state sulfur atoms exhibit electrophilic behavior. Little, however, is known regarding the selectivity of $S(^1D)$ atoms towards the double bond.

Recently, also, the relative rates of addition of sulfur atoms (mixture of $S(^1D)$ and $S(^3P)$ atoms) to olefins were measured (77). Maximum values for the relative rate constants of addition of $S(^1D)$ atoms to the double bond were found to be 1, 2.9 and 7.5 for ethylene, propylene and isobutylene, as compared to 1, 6.8 and 50 for $S(^3P)$ addition. Since the relative importance of $S(^1D)$ and $S(^3P)$ atoms cannot be evaluated from these results only maximum values for the relative rate constants can be determined. It is evident that $S(^1D)$ atoms are less selective than $S(^3P)$ but no quantitative measure of the selectivity can be made.

It was felt that additional information on the reactivity of $S(^1D)$ with olefins may be obtained by observing the relative reactivity of $S(^1D)$ atoms towards C-H and C=C bonds in a series of methyl substituted ethylenes. Propylene (71) the 2-butenes and isobutene (26) have already been studied and the series was extended to

include trimethyl and tetramethylethylene. The results are shown in Table X. The percentage insertion into the methyl groups is seen to increase almost linearly with the number of methyl groups, i.e., the rate of insertion per C-H bond remains almost constant. Since the rate of insertion per C-H bond should not be greatly influenced by the number of methyl groups in the molecule, the relative reactivity of the π bonds in the series can be estimated. This turns out to be approximately constant.

This indicates that any selectivity that the $S(^1D)$ atom possesses must be quite small. The possibility of steric hindrance, resulting in an apparent lack of increased reactivity with the double bond, must not be overlooked. It has been suggested that a small steric hindrance effect is present in the reactions of $S(^3P)$ atoms with α, β -substituted olefins. If the same effect is present for $S(^1D)$ atoms the observed lack of selectivity may not represent the true reactivity.

The Effect of Perfluorination on the Reactivity of Sulfur Atoms With Olefins.

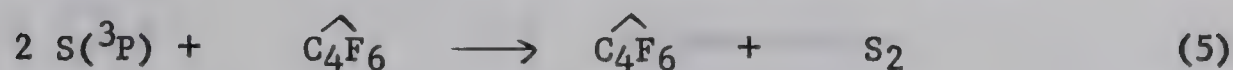
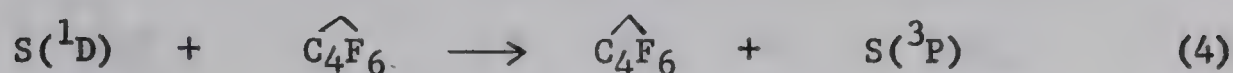
The photolysis of COS in the presence of perfluorocyclobutene resulted in a decrease in CO production with increasing substrate pressure. No carbon-sulfur compound was produced in the reaction. The major product was elemental sulfur with a small percentage of carbon containing non-volatile solid. The large decrease in CO formation in the COS-perfluorocyclobutene system may therefore be due to efficient third body recombination of $S(^3P)$ atoms in the presence

TABLE X

PERCENTAGE INSERTION INTO METHYL C-H BONDS
FOR A SERIES OF METHYLATED ETHYLENES

Compound	% Insertion into CH ₃ group
CH ₃ CH=CH ₂	20%
<u>cis</u> CH ₃ CH=CHCH ₃	30%
<u>trans</u> CH ₃ CH=CHCH ₃	30%
(CH ₃) ₂ C=CH ₂	30%
(CH ₃) ₂ C=CHCH ₃	40%
(CH ₃) ₂ C=C(CH ₃) ₂	50%

of $\widehat{\text{C}_4\text{F}_6}$. The overall mechanism appears to include the following steps:



The percentage recombination of the initially-produced sulfur atoms is given by the expression:

$$\% \text{ recombination} = \frac{2(\text{R}^0(\text{CO}) - \text{R}(\text{CO}))}{\text{R}^0(\text{CO})} \times 100$$

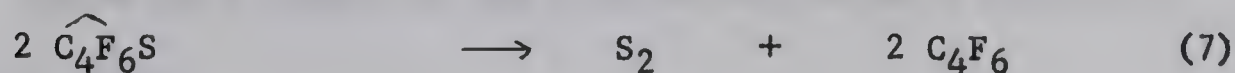
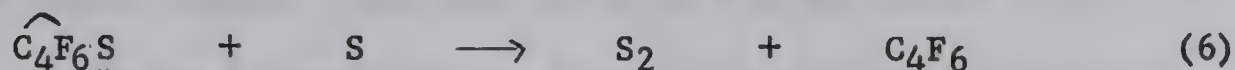
Since some polymerisation, resulting in solid formation, does occur, this term actually represents the percentage of sulfur atoms disappearing by both recombination and polymerisation.

At 1000 torr of added substrate the percentage recombination is 90%. Under identical conditions CO_2 gave a value of ca. 25% recombination (70). Perfluorocyclobutene is therefore approximately 3.6 times more efficient as an apparent third body for the recombination of sulfur atoms than is CO_2 , although both of these compounds display roughly the same ability for deactivating excited sulfur atoms.

The increased ability of the perfluorocyclobutene in the recombination process may arise from some process other than a simple third body recombination. This is convincingly shown by the technique of flash photolysis-kinetic mass spectrometry where a $\widehat{\text{C}_4\text{F}_6}\text{S}$ adduct was observed as a reaction product. The $\widehat{\text{C}_4\text{F}_6}\text{S}$ product was stable

under these conditions but its disappearance is indicated by the lack of a $\widehat{\text{C}_4\text{F}_6}\text{S}$ product in the static system.

As elemental sulfur was the major product of the reaction it is reasonable to propose the following mode of $\widehat{\text{C}_4\text{F}_6}\text{S}$ disappearance:



The two reactions leading to polymerisation are small compared to the S_2 producing reactions.

Sulfur formation in this reaction is probably due to (a) third body recombination and (b) reactions involving a short-lived sulfur adduct of $\widehat{\text{C}_4\text{F}_6}$ as a reaction intermediate. At present there is no way of estimating the relative importance of these two steps although both reactions are probably taking place in this system.

The reactions of sulfur atoms with C_2F_4 have recently been observed (70) and here also no sulfur product was found. Teflon, resulting from the S atom-initiated polymerisation of C_2F_4 , was, however, observed to be formed in the reaction. Perfluorocyclobutene was found not to undergo a similar polymerisation to any measureable extent.

A rough estimate of the reactivity of $\widehat{\text{C}_4\text{F}_6}$ compared to cyclopentene may be made from the data on the addition of $\widehat{\text{C}_4\text{F}_6}$ to the COS-cyclopentene system. Addition of a seven-fold excess of perfluorocyclobutene resulted in a ca. 20% decrease in the yield of

C_5H_8S products. This would indicate that $\widehat{C_4F_6}$ is at least 25 times less reactive toward sulfur atoms than cyclopentene. This dramatic decrease in the reactivity is not unexpected in view of the inertness of the C-F bonds towards insertion and also the decreased reactivity of the π system as a result of the electron-withdrawing effect of the fluorine atoms.

CHAPTER IV

REACTIONS OF SULFUR ATOMS WITH CHLORINE CONTAINING COMPOUNDS

A. Reactions of sulfur atoms with vinyl chloride

- i. Results.
- ii. Discussion.

B. Reactions of sulfur atoms with cis and trans- 1,2-dichloro ethylenes.

- i. Results.
- ii. Discussion.

C. Reactions of sulfur atoms with chloro alkanes

- i. Results.
- ii. Discussion.

RESULTS

A. Vinyl Chloride

When carbonyl sulfide was photolysed with vinyl chloride, in low conversion runs, two gas chromatographically separable products were formed with relative retention times 1.00(I):1.19(II) on an 8 foot T.C.P. column. The products were shown by their mass spectra each to have a molecular weight of 94.

Compound I was found to be a chlorovinyl mercaptan. However since it was a minor product, its exact structure could not be determined. This compound may possibly be a mixture of two mercaptans, cis and trans-2-chlorovinyl mercaptans, ClCH=CH-SH .

Compound II was identified as the vinyl chloride episulfide.

The product rates, as a function of vinyl chloride pressure, are shown in Table XI and Figure 16. It is seen that the products increase with increasing substrate pressure and reach a maximum value at substrate pressures greater than 300 torr. The ratio $R(\text{mercaptan})/R(\text{episulfide})$ is pressure dependent, reaching a limiting maximum value of 0.19 at high pressures of vinyl chloride. The rate of formation of CO decreases with increasing olefin pressure and at the highest pressure used (772 torr) it is seen to fall slightly below $R^0(\text{CO})/2$. This decrease to a value somewhat less than $R^0(\text{CO})/2$ is probably due to competitive light absorption by the vinyl chloride in this high pressure region.

The product rates were also studied as a function of added CO_2 . Table XII and Figure 17 show the same type of effect observed for all olefins. The episulfide increased with CO_2 pressure while the mercaptan yield remained constant up to 1000 torr of added CO_2 and then began to

TABLE XI

VARIATION IN PRODUCT YIELDS WITH VINYL CHLORIDE PRESSUREIN THE COS - VINYL CHLORIDE SYSTEM^aRates, μ moles/30 min.

$P(C_2H_3Cl)$ torr	CO	$CO^O - CO$	C.V.M. ^b	ES	Total C_2H_3ClS	$\frac{CVM}{ES}$	% Recovery ^c
44.8	4.53	2.90	0.13	0.92	1.05	0.14	36
74.9	4.43	3.09	0.17	1.21	1.38	0.14	45
101.2	4.25	3.18	0.19	1.27	1.46	0.15	46
152.3	4.02	3.41	0.22	1.35	1.57	0.16	46
253.3	3.84	3.59	0.24	1.32	1.56	0.18	44
609.2	3.56	3.87	0.27	1.44	1.71	0.19	44
772.0	3.44	3.99	0.27	1.43	1.70	0.19	43

a. $P(COS) = 100$ torr: Exposure time = 30 min.

b. Chlorovinyl mercaptan.

c. In terms of $R^O(CO) - R(CO)$.

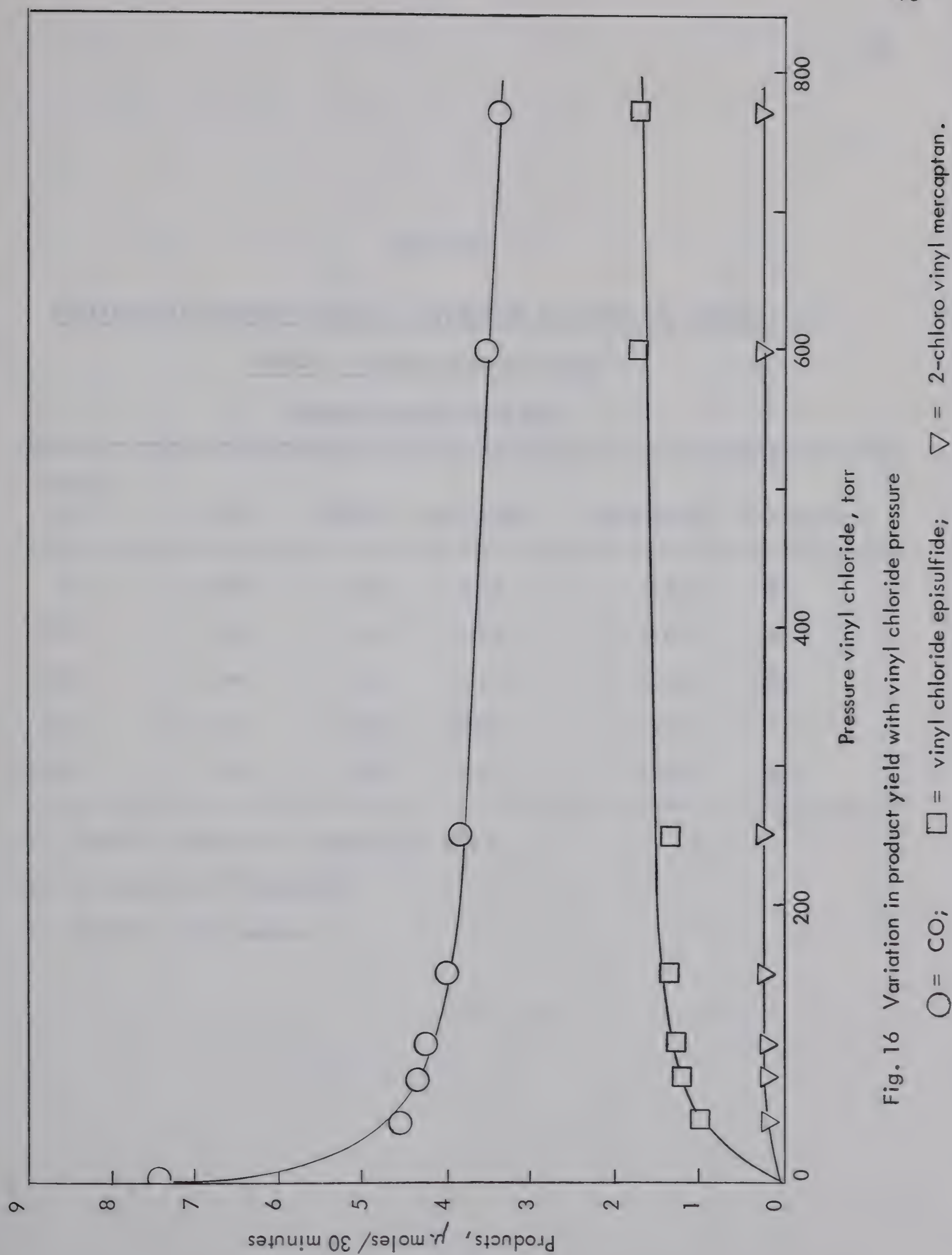


Fig. 16 Variation in product yield with vinyl chloride pressure

TABLE XII

VARIATION IN PRODUCT YIELDS AS A FUNCTION OF ADDED CO₂ PRESSURE IN
THE COS - VINYL CHLORIDE SYSTEM^a

Results, μ moles/30.0 min.

P(CO ₂) torr	CO	CO ^O -CO	mercaptan	episulfide	% recovery ^b
0	3.76	3.07	0.19	1.25	47
295	3.67	3.16	0.23	1.67	60
527	3.64	3.19	0.25	1.72	62
945	3.74	3.09	0.24	1.96	71
1366	3.74	3.09	0.17	1.93	68

a. P(COS) = 100 torr; P(C₂H₃Cl) = 235.5

b. In terms of R^O(CO)-R(CO).

c. R^O(CO) = 6.83 moles.

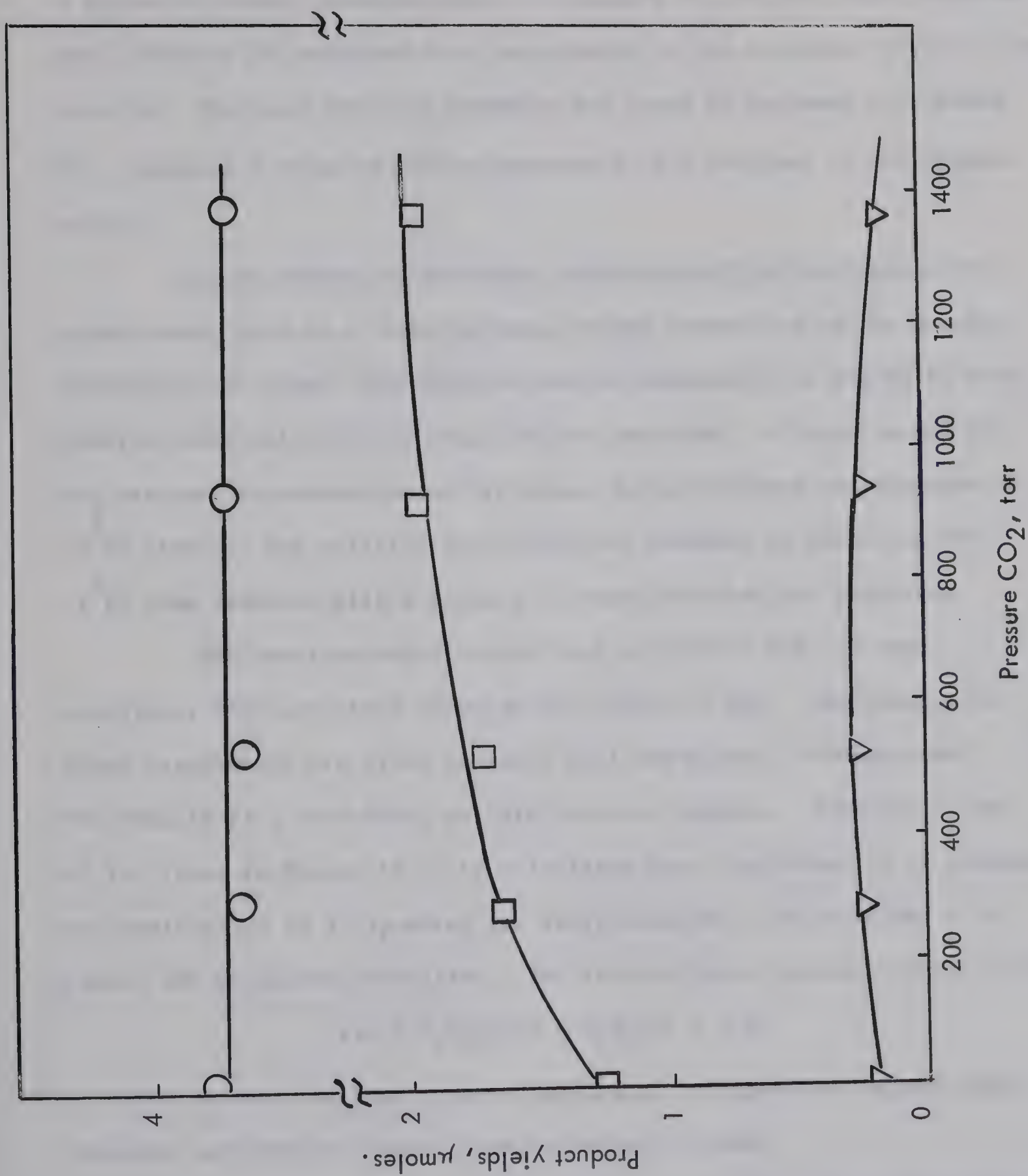


Fig. 17 Product formation as a function of added CO_2

decrease. The yield of the mercaptan can be reduced to nearly zero with a higher CO_2 /vinyl chloride ratio. A mixture of 150 torr vinyl chloride and 1200 torr CO_2 resulted in a suppression of the mercaptan yield to less than 2%. The total yield of products was found to increase with added CO_2 , reaching a value of 70% as compared to 45% obtained in the absence of CO_2 .

In an attempt to determine the effect of an electronegative substituent, such as a chlorine atom, on the reactivity of the molecule towards sulfur atoms, the relative rate of reactivity of the $\text{S}(^3\text{P})$ atom towards vinyl chloride and propylene was measured. A large excess of CO_2 was used to produce the $\text{S}(^3\text{P})$ atoms, by collisional deactivation of $\text{S}(^1\text{D})$ atoms. The relative reactivity was measured by observing the $\text{S}(^3\text{P})$ atom reaction with a mixture of vinyl chloride and propylene.

The reaction mixture consisted of 50 torr COS, 30 torr propylene, 150 torr vinyl chloride and 1200 torr CO_2 . The results of these experiments are given in Table XIII and Figure 18 which shows the results of a time study on this reaction mixture. From the slopes of the lines in Figure 18 it is calculated that the formation of products per μmole of CO is $0.33 \mu\text{moles}$ for vinyl chloride episulfide and $0.34 \mu\text{moles}$ for propylene episulfide. The relative rate constant ratio is then:

$$k(\text{S} + \text{C}_3\text{H}_6)/k(\text{S} + \text{C}_2\text{H}_3\text{Cl}) = 5.0$$

In order to make the results more meaningful a comparison between vinyl chloride and ethylene rather than propylene is made.

The relative rate for the reaction of $\text{S}(^3\text{P})$ atoms with ethylene and propylene has been previously measured (77) and the reactivity found to be propylene/ethylene = 6.8. Using this value, the value for the relative reactivity of $\text{S}(^3\text{P})$ atoms towards vinyl chloride and ethylene is

TABLE XIII

PRODUCT YIELDS IN THE VINYL CHLORIDE-PROPYLENE SYSTEM^aYield in μ moles

Time	CO	$R^O(CO)-R(CO)$	VCES ^b	PES ^c	PES x 5	% Yield ^d
10	2.25	1.75	0.70	0.77	3.85	84
10	2.16	1.84	0.71	0.75	3.75	79
15	3.11	2.89	1.13	1.08	5.40	76
20	4.15	3.85	1.46	1.40	7.00	74
30	6.07	5.90	2.17	2.21	11.05	74
40	8.00	8.00	2.66	2.72	13.60	74

a. COS = 50 torr., vinyl chloride = 150 torr., propylene = 30 torr

CO₂ = 1190 torr., $R^O(CO)$ = 24.12 μ moles/hour.

b. Vinyl chloride episulfide.

c. Propylene episulfide.

d. In terms of $R^O(CO)-R(CO)$.

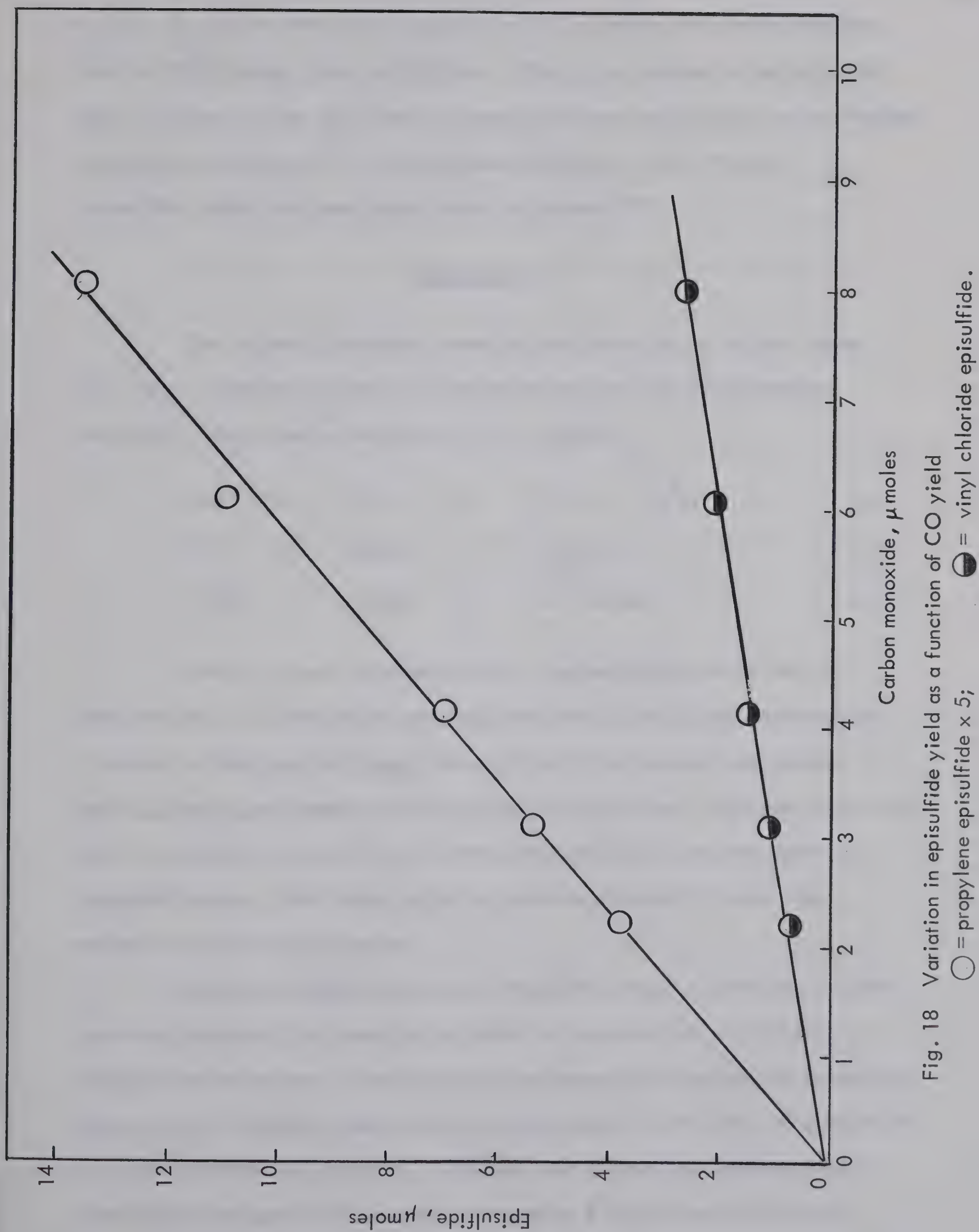
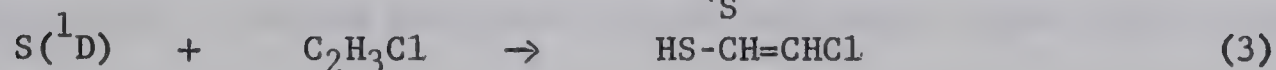
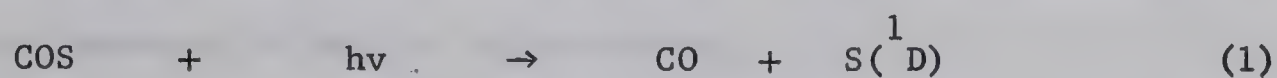


Fig. 18 Variation in episulfide yield as a function of CO yield

= 1.4. It can be seen that vinyl chloride is appreciably more reactive towards $S(^3P)$ atoms than is ethylene. This is a minimum value for this ratio in view of the fact that although ethylene episulfide can be obtained in yields approaching 95%, the optimum yield for vinyl chloride episulfide under the same conditions is around 70%.

DISCUSSION

The primary products formed in the reaction of sulfur atoms with vinyl chloride are vinyl chloride episulfide and 2-chlorovinyl mercaptan. The primary reactions can be written:



The G.C. peak corresponding to the mercaptan could not be resolved and it is not known whether this peak is only one mercaptan or a mixture of the cis and trans forms of the 2-chlorovinyl mercaptan. Both cis and trans isomers are formed in the COS-vinyl fluoride system (70) but it is not necessary that the same reactions occur in the COS-vinyl chloride system. The larger chlorine atom may markedly change the mercaptan product distribution.

Figure 16 shows the product distribution as a function of vinyl chloride pressure; the reaction proceeds in a manner characteristic of all COS-olefin systems. The CO yield decreases with increasing substrate pressure. At the same time there is an increase in the rate of production of sulfur-containing products. When all the initially produced sulfur atoms are scavenged $R(\text{CO})$ reaches a value of $R^0(\text{CO})/2$ and the rate of

product formation reaches a constant maximum value.

The reactions of sulfur atoms with hydrocarbon olefins show essentially the same quantitative features for all the olefins studied. Two general features are (a) product yields are found to vary between ca. 70 to 95% and (b) $R(M)/R(E)$ varies from ca. 0.50 to 1.00. The COS-vinyl chloride system differs in that the optimum yield observed in the reaction is 46% and the maximum value for the ratio $R(M)/R(E)$ is 0.19. There are several factors that could be responsible for this change from the hydrocarbon systems. One possibility is the decomposition of the 2-chlorovinyl mercaptan. Loss of this product would result in a decrease of both of these values.

Saturated β -chloro mercaptans are shown to decompose by HCl elimination (114). The low mercaptan yields may result from the following decomposition:



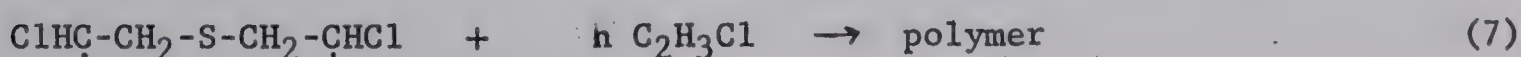
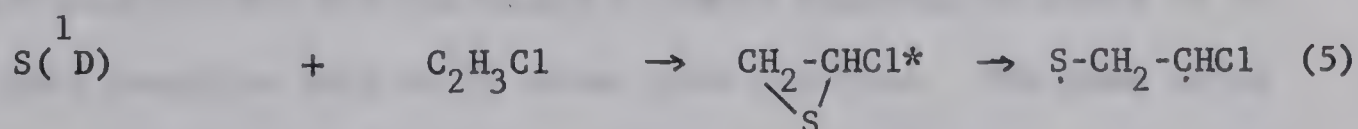
The sulfur adduct, $\text{C}_2\text{H}_2\text{S}$ may be similar to that proposed in the reaction of $\text{S}(^1\text{D})$ with acetylene. No $\text{C}_2\text{H}_2\text{S}$ product could be isolated in the COS-acetylene system, indicating that this adduct does not result in a stable product. In the acetylene system this intermediate leads to polymerisation and this is probably its fate if formed in this reaction.

The instability of the mercaptan product is also indicated by the CO_2 study, the results of which are shown in Figure 17. It can be seen that with increasing CO_2 pressure the episulfide rises and the mercaptan yield, at high CO_2 pressures, decreases. Unlike the hydrocarbon olefin systems, however, the mercaptan yield first increases slightly with CO_2 pressure and then at pressures greater than ca. 1000

torr of added CO_2 it slowly decreases. Even though added CO_2 results in $\text{S}(^1\text{D})$ to $\text{S}(^3\text{P})$ conversion, (and mercaptans are formed only from $\text{S}(^1\text{D})$ atoms), the mercaptan formation increases slightly. This indicates that CO_2 functions first to stabilise collisionally the initially formed hot mercaptan. At the maximum of the curve the additional stabilisation by the CO_2 is just equal to the decrease in mercaptan formation from the $\text{S}(^1\text{D})$ to $\text{S}(^3\text{P})$ conversion. With additional CO_2 the mercaptan yield decreases and approaches zero at very high CO_2 pressures.

A second factor that may be responsible for the low $\text{R(M)}/\text{R(E)}$ ratio is an increased efficiency of vinyl chloride in bringing about electronic relaxation of $\text{S}(^1\text{D})$ atoms to $\text{S}(^3\text{P})$ atoms. If vinyl chloride is more efficient in this process then, since $\text{S}(^3\text{P})$ atoms can react to produce only episulfide, the ratio $\text{R(M)}/\text{R(E)}$ would be lower than in other cases.

The overall yield of products is seen to increase from 46% to 70% when 1350 torr of CO_2 is added to the reaction system. This increased yield is partly due to increased stabilisation of the hot episulfide formed but mainly arises from increasing the rate of $\text{S}(^3\text{P})$ atom reactions, which are less exothermic, relative to the $\text{S}(^1\text{D})$ reactions. It has been shown that thiodimethylene radicals add to double bonds resulting in polymerisation (26). In the absence of CO_2 singlet sulfur atoms add to vinyl chloride producing hot episulfide molecules. These, if not stabilised, may undergo ring opening from C-S bond rupture and the biradical formed may react with substrate molecules resulting in polymer formation.



Addition of CO_2 results in reaction of $\text{S}(^3\text{P})$ rather than $\text{S}(^1\text{D})$ atoms with vinyl chloride. The episulfide product has 26 kcal/mole less energy when formed by $\text{S}(^3\text{P})$ atom addition and is therefore more easily stabilised. The biradical addition reaction resulting in polymerisation is also decreased when CO_2 is added since CO_2 will enhance ring closure of the biradical.

Recent studies have shown that $\text{S}(^3\text{P})$ atoms react with mono-olefins in the following order of relative reactivity: ethylene < propylene < 1-butene < trans-2-butene < isobutylene < 2-methyl-1-butene (77).

The electron-releasing alkyl groups enhance, by induction, the electron density of the double bond in each of these olefins, making it more susceptible to attack by electron-seeking or electrophilic reagents. Since the order of reactivity of $\text{S}(^3\text{P})$ atoms follows the increased electron density of the π -system, $\text{S}(^3\text{P})$ atoms are regarded as electrophilic reagents. Other members of the oxygen group of elements show similar electrophilic character, namely $\text{O}(^3\text{P})$ (100) and $\text{Se}(^3\text{P})$ (55) atoms.

Since electron-releasing groups increase the reactivity of a molecule towards $\text{S}(^3\text{P})$ atoms, it would be expected that groups showing a negative inductive effect would exhibit the opposite effect. Halogen atoms are known to be electron-withdrawing groups and have been shown to decrease the reactivity of benzene towards electrophilic substitution. Replacement of a H-atom of ethylene by a chlorine atom would therefore be expected to result in a decreased reactivity towards $\text{S}(^3\text{P})$ atoms. The results are contrary to this reasoning as vinyl chloride is found to be 1.4 times more reactive with $\text{S}(^3\text{P})$ atoms than ethylene. The same trend in reactivity was also found for the reaction of $\text{Se}(^3\text{P})$ atoms with vinyl

chloride (55) where the relative rate of reactivity was found to be $k(\text{Se} + \text{vinyl chloride})/k(\text{Se} + \text{ethylene}) = 1.3$.

These results show quite conclusively that the reactivity of a molecule cannot be predicted simply on the grounds of the electron density of the π -system of the double bond, although in the hydrocarbon olefin system this general hypothesis seems to hold true. Since the reaction deals with electrophilic or electron-seeking reagents, the reactivity of a molecule should be considered from the point of its overall basicity or ability to give up electrons. Quantitatively, the ease with which a molecule will give up an electron is a function of the ionisation potential of the molecule. Table XIV lists the ionisation potentials for a number of olefins that have been studied in the COS-olefins systems. It is clearly seen that, on the basis of ionisation potential, vinyl chloride would be expected to be more reactive towards electrophilic reagents. A plot of ionisation potential vs. $\log k$ for $S(^3P)$ atom addition to olefins is shown in Figure 19. For the hydrocarbon olefins, very close correlation between reactivity and ionisation potential is found. The molecule showing the largest deviation from the line is vinyl chloride. It is noticed, however, that the predicted reactivity, based on the ionisation potential, is even larger than that actually observed in the reaction. This decrease in expected reactivity can now be attributed to the strong electron-withdrawing effect of the chlorine atom, moderated by the resonance hybrid structure $\text{H}_2\overset{-}{\text{C}} - \overset{+}{\text{CH}} = \text{Cl}$, the contribution of which is ca. 6%.

TABLE XIV

RELATIVE RATES OF ADDITION OF S(³P) ATOMS TO OLEFINS

Olefin	k rel. ^a	I.P. (ev.) ^c
ethylene	1.00	10.62
vinyl chloride ^b	1.4	9.995
propylene	6.8	9.84
1-butene	10	9.76
1-pentene	10	9.67
cyclopentene	18	9.27
<u>trans</u> -2-butene	20	9.27
<u>cis</u> -2-butene	16	9.34
isobutylene	50	9.26
2-methyl-1-butene	56	9.20

a. $k \text{ rel.} = k(\text{S} + \text{olefin})/k(\text{S} + \text{C}_2\text{H}_4)$

values taken from reference (77).

b. this work.

c. values taken from reference (78).

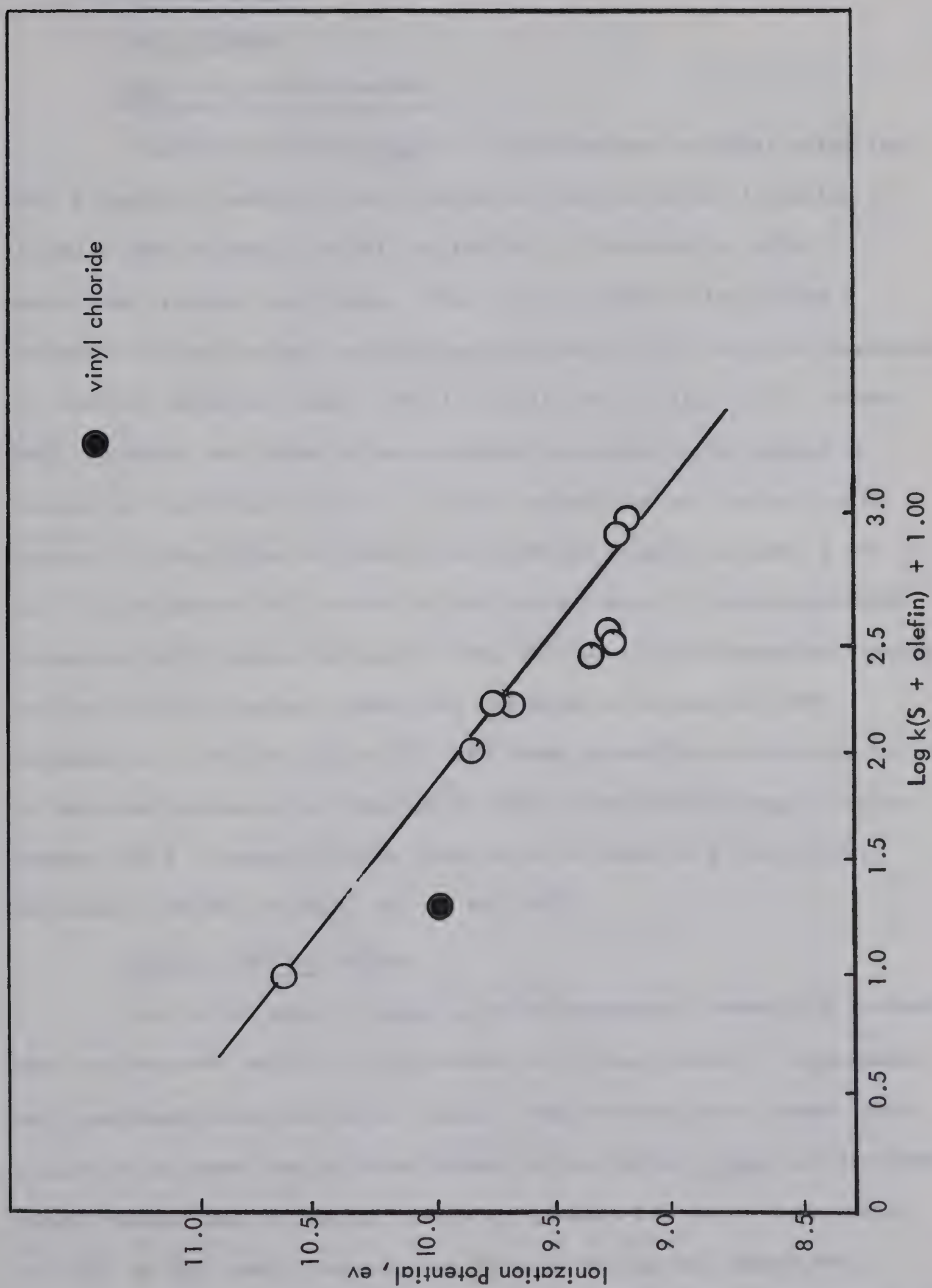


Fig. 19 Ionization Potentials vs $\text{Log } k$ for $S(^3P)$ Atom Addition to Olefins.

B. 1,2-DICHLOROETHENES

1. Static System

Trans - 1,2-dichloroethene

Photolysis of COS-trans-1,2-dichloroethene mixtures using the 2490 Å source at moderate total pressures resulted in the formation of CO and a dark polymeric deposit on the cell. No volatile sulfur-containing products were found. When CO₂ was added to the system a condensable fraction was isolated and resolved by G.C. into two components of relative retention times 1.00(I):5.30(II) on a 0.5 ft. T.C.P. column. Both compounds were shown by mass spectral analysis to correspond to isomers of the formula C₂H₂Cl₂S. Since episulfides are the only major products arising from the photolysis of COS-CO₂-olefin systems, I and II can only be geometrical isomers of the episulfide of 1,2-dichloroethene. By analogy with results obtained in the COS-CO₂-1,2-dichloroethene system and the COS-CO₂-2-butene system (26) the trans structure has been assigned to I, and the cis to II. The trans episulfide represented ca. 90% of the total products (as compared to 98% in the COS-CO₂-trans-2-butene system (26)). Product yields, calculated in terms of R^O(CO)-R(CO), increased with CO₂ pressure, to ca. 60 - 80%.

Cis-1,2-dichloroethene

As in the case of trans-1,2-dichloroethene, condensible products were not observed unless a large excess of CO₂ was present. Experiments were performed using the Hg-arc source. Two products were formed, which eluted at the same time as those formed in the COS-CO₂-trans-1,2-dichloroethene system, and by similar reasoning, product II, which represented ca. 80% of the total products, was taken to be the cis isomer and I the trans isomer. Product yields were ca. 10-20% at high pressures of CO₂.

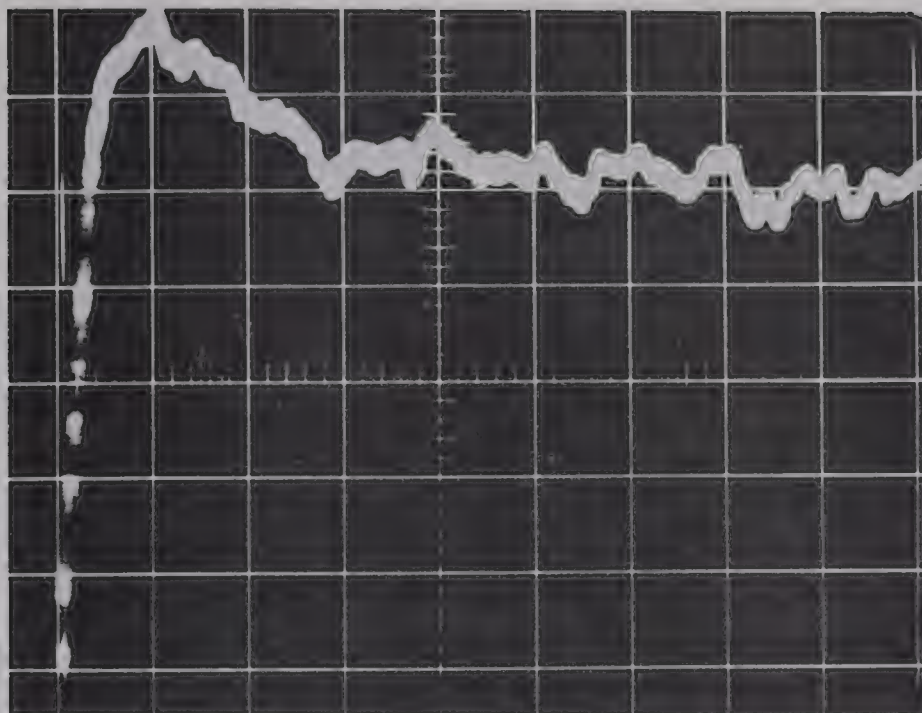
2. Flash photolysis-kinetic mass spectrometry.

The reaction of sulfur atoms with trans-1,2-dichloroethene was also studied by flash photolysis-kinetic mass spectrometry. The reaction cell contained 400 microns of COS and 800 microns of trans-1,2-dichloroethene. The appearance and decay of mass 128, corresponding to $\text{C}_2\text{H}_2\text{Cl}_2^{35}\text{S}$, was monitored and the results are shown in Figures 20-24. The signal has been corrected to account for the normal bleed-out of products through the leak. Unlike the signal obtained for a stable product (Figure 25), i.e., levelling off to a stable maximum, the signal for $\text{C}_2\text{H}_2\text{Cl}_2\text{S}$ rises rapidly to a maximum, decays very rapidly to a value somewhat less than the maximum and then remains constant with time. Furthermore, the rapidly decaying signal, between the maximum and 50 milliseconds, is less pronounced with each successive flash as indicated in Figures 20-23.

DISCUSSION

The reaction of $\text{S}(^1\text{D})$ atoms with 1,2-dichloroethene fails to produce a stable volatile sulfur containing product in either the static system or the method of flash photolysis-kinetic mass spectrometry. The latter method is, however, capable of detecting a short-lived $\text{C}_2\text{H}_2\text{Cl}_2\text{S}$ adduct which disappears rapidly by decomposition to smaller fragments or by further reaction with formation of a higher molecular weight product. The persistence of the 128 signal, after the initial rapid drop cannot be due to a free stable $\text{C}_2\text{H}_2\text{Cl}_2\text{S}$ product but may be due to a cracking fragment of a new product. This new product must contain at least one $\text{C}_2\text{H}_2\text{Cl}_2\text{S}$ fragment plus one or more $\text{C}_2\text{H}_2\text{Cl}_2\text{S}$ or $\text{C}_2\text{H}_2\text{Cl}_2$ groups.

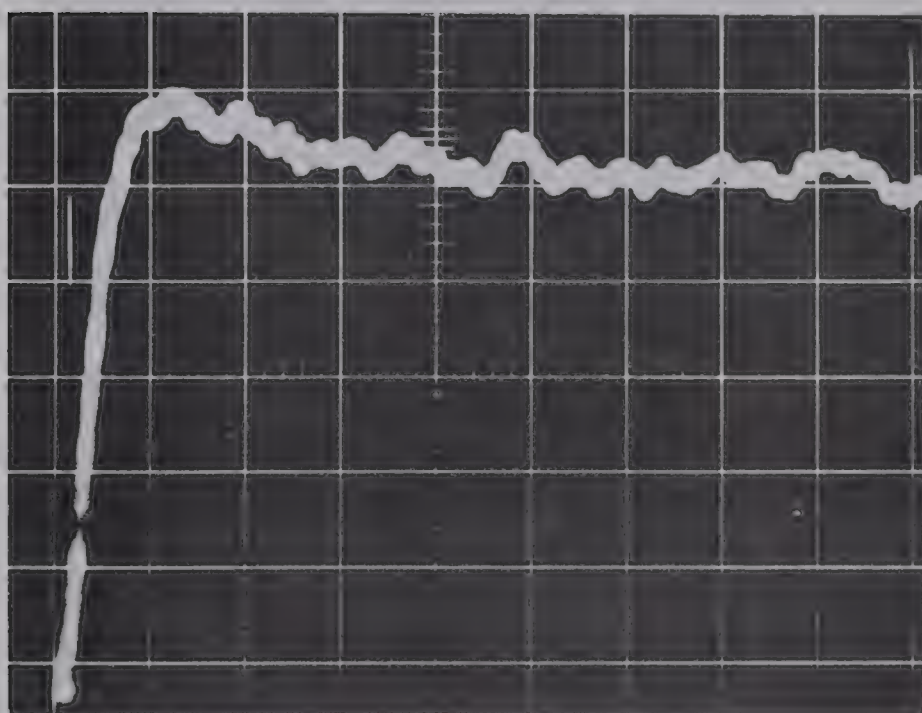
50.0
Millivolts
per div.



10.0 Milliseconds per div.

Fig. 20 Mass 128. $C_2H_2Cl_2S$
First signal.

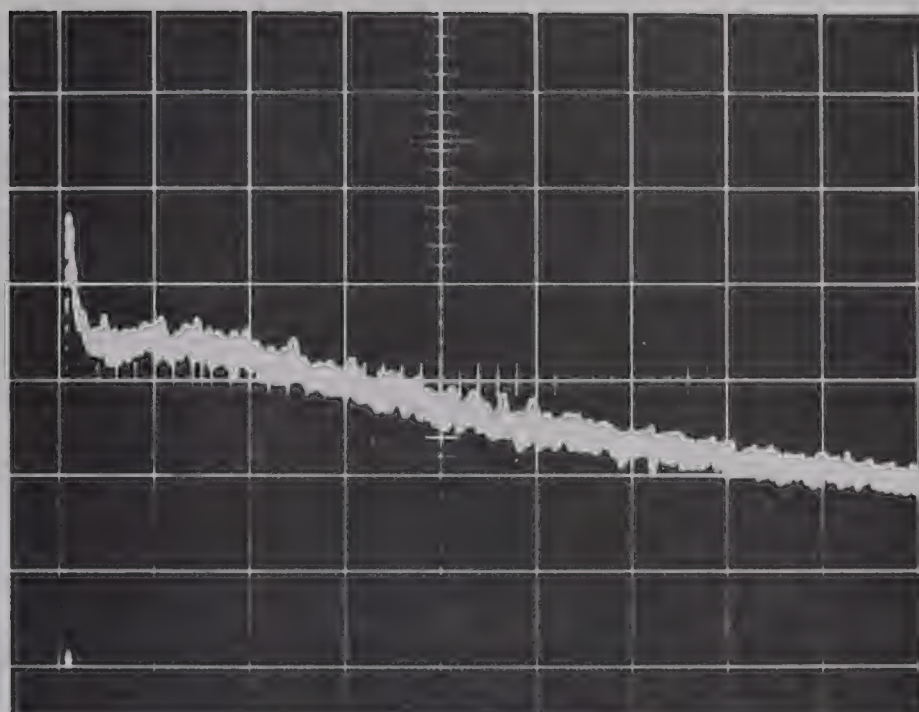
50.0
Millivolts
per div.



10.0 Milliseconds per div.

Fig. 21 Mass 128, $C_2H_2Cl_2S$
After several flashes.

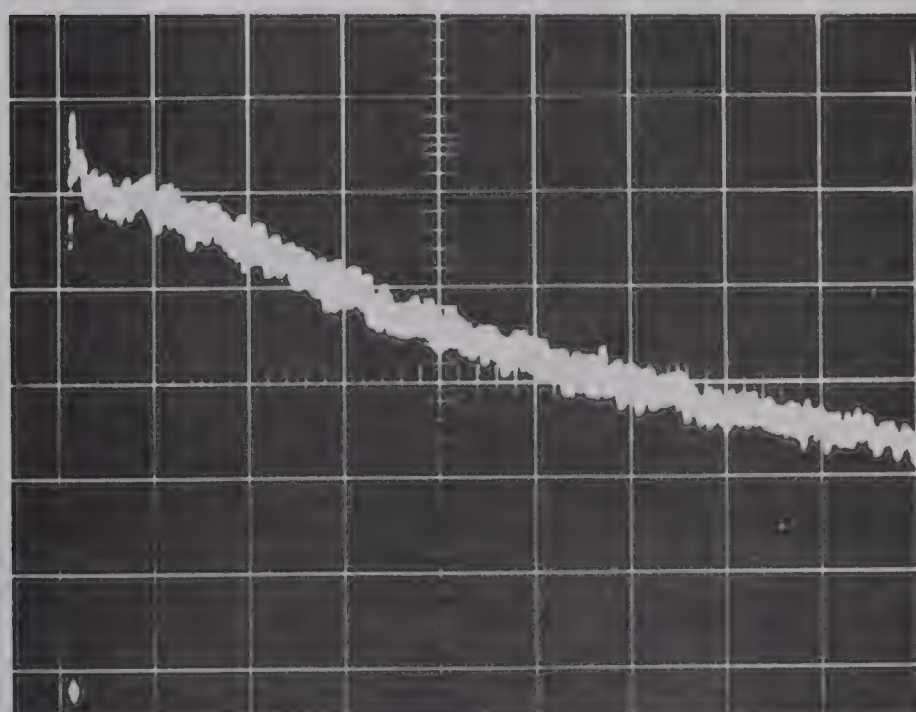
0.1 Volt
per div.



0.2 Seconds per div.

Fig. 22 Mass 128, $\text{C}_2\text{H}_2\text{Cl}_2\text{S}$
First signal

0.1 Volt
per div.



0.2 Seconds per div.

Fig. 23 Mass 128, $\text{C}_2\text{H}_2\text{Cl}_2\text{S}$
After several flashes.

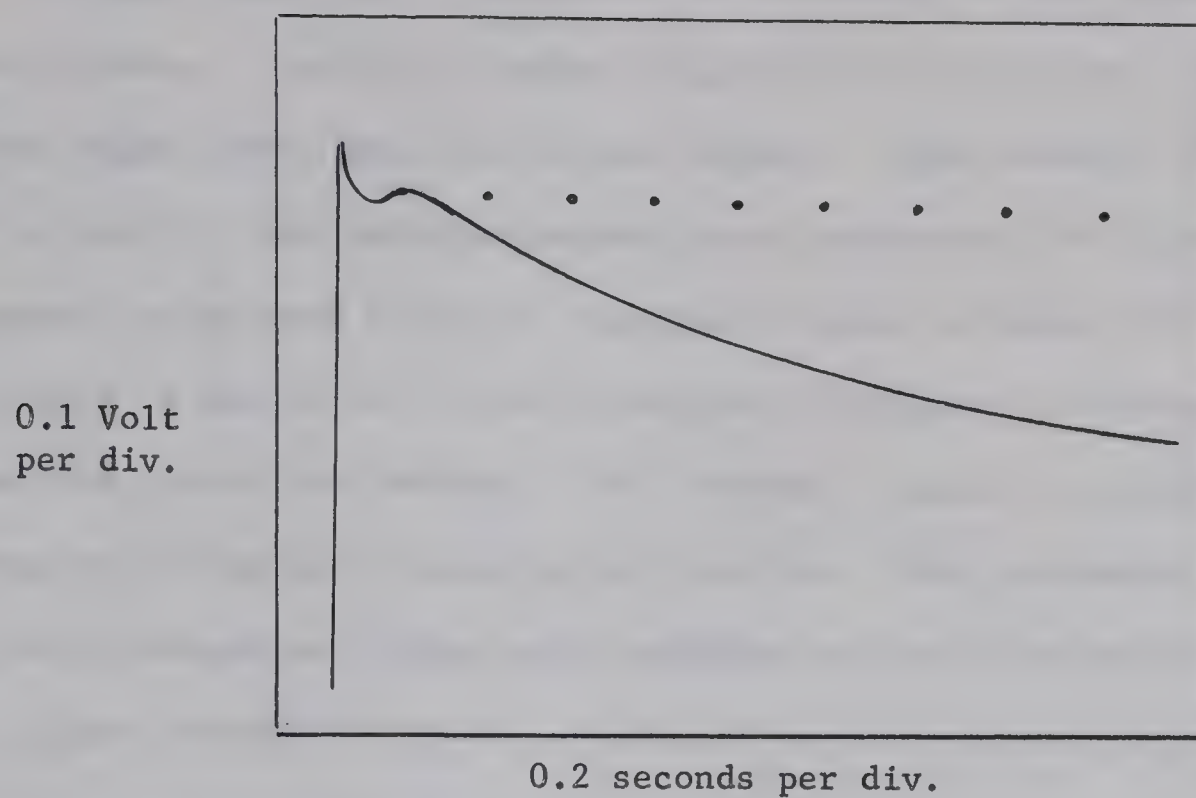


Fig. 24 Mass 128, $C_2H_2Cl_2S$

Dotted line corrected for
bleed-out.

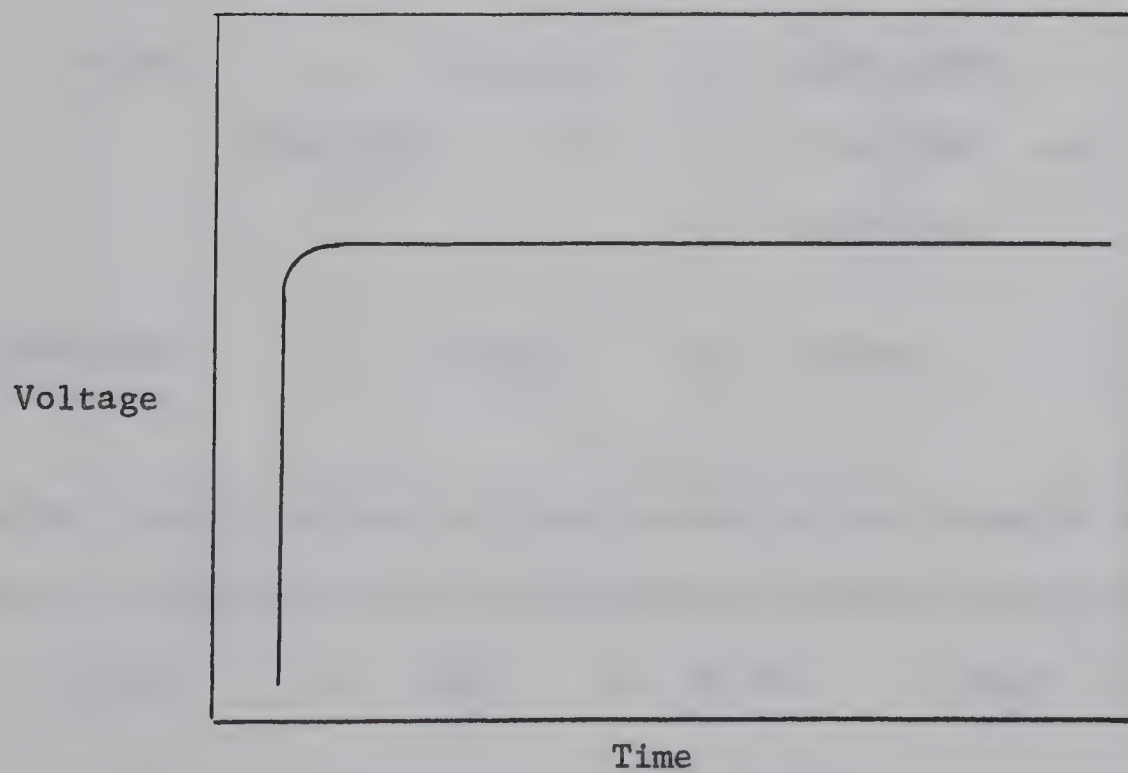
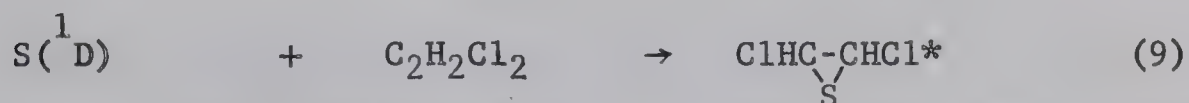
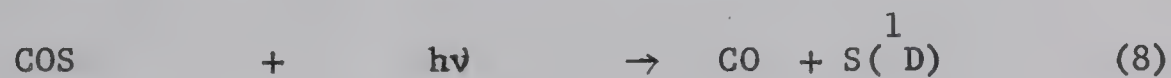


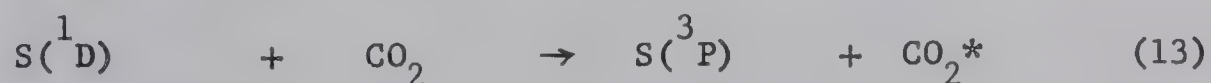
Fig. 25 Normal signal for stable
volatile product, after bleedout
correction.

Polymer formation is suggested by the change in the signal with successive flashes. The first flashes (Figures 20 and 22) show a sharp drop in the signal after the initial peak signal. After several flashes (Figures 21 and 23) this decrease becomes less pronounced. The total signal appears to be made up of two components shown in Figure 25a. The primary signal is due to the initial formation of $C_2H_2Cl_2S$ and decreases rapidly as the product polymerises. The secondary signal is produced by cracking of the polymer formed in the reaction. The phenomenon observed with successive flashes must therefore be due to an additional secondary signal caused by removal of solid from the cell wall by the high intensity photolytic flash.

The overall reaction of sulfur atoms with 1,2-dichloroethenes, in the static system, must include the following steps:



Addition of CO_2 (static system) is found to aid in the formation of stable products, probably due to the following additional reactions:



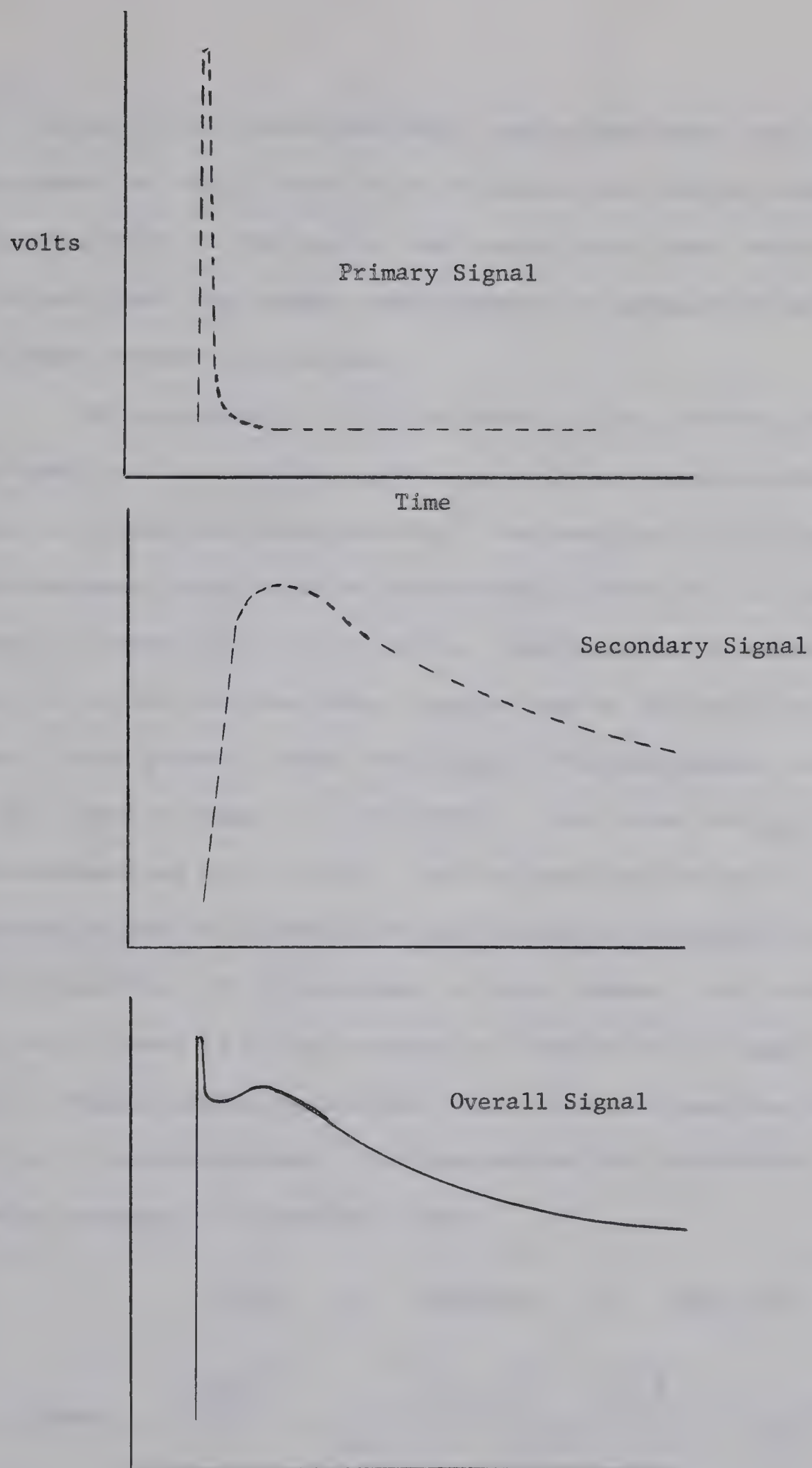
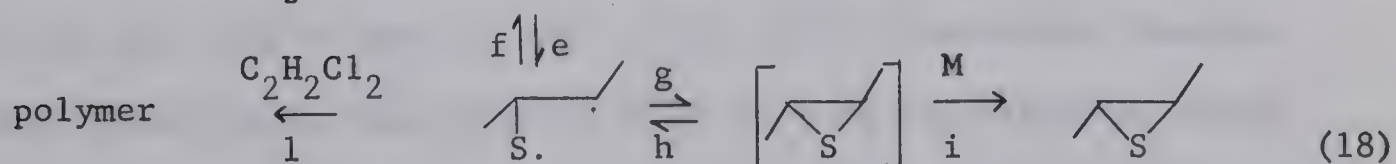
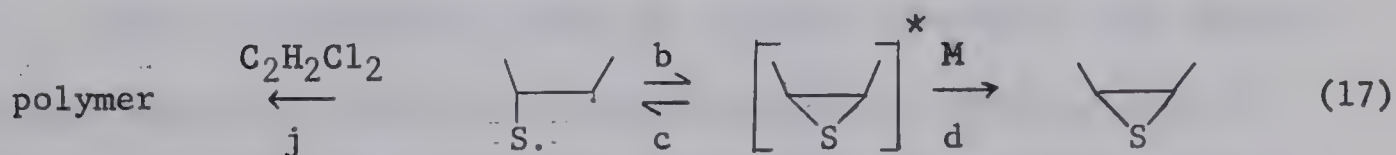
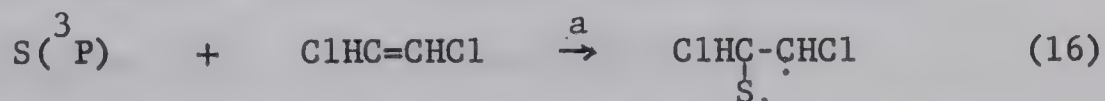


Fig. 25a. Components of the $C_2H_2Cl_2S$ Signal.

Step 9 is ca. 85 kcal./mole exothermic and unless stabilised immediately this product may easily open to the biradical and undergo further reaction. Addition of $S(^3P)$ to the double bond results in a lower exothermicity of ca. 60 kcal./mole and product stabilisation is enhanced by the presence of a large pressure of inert gas.

In the presence of a large excess of CO_2 , previous studies have shown that the reactive species is $S(^3P)$ and reaction with olefins results in episulfide formation only. The reaction of $S(^3P)$ with 1,2-dichloroethenes shows definite stereospecific behavior; only one major product is formed with each substrate. Configuration is retained to the extent of ca. 90% with the trans compound and ca. 80% with the cis isomer. While product yields with trans-1,2-dichloroethene are relatively high (60 - 80% in terms of $R^O(CO)-R(CO)$), the yields for cis-1,2-dichloroethene are only 10-20%. This low yield may be due to: (a) increased reactivity of the cis biradical or (b) instability or cis-1,2-dichloroethene episulfide. It is important to note, however, that rotation about the C-C bond is a slow process, as revealed by the small amount of trans-1,2-dichloroethene episulfide formed from the reaction of $S(^3P)$ with cis-1,2-dichloroethene. The observations are illustrated in the following sequence of elementary steps:



The initial formation of a triplet biradical, from addition of $S(^3P)$ to the double bond, is required by spin conservation. Three reaction paths are then open to the biradical: (a) ring closure yielding the episulfide, (b) isomerisation and (c) reaction with substrate resulting in polymer formation.

The high yield of trans-1,2-dichloroethene episulfide from trans-1,2-dichloroethene indicates large values for k_g and M_k ; while k_1 must necessarily be small.

With cis-1,2-dichloroethene the product yield was found to be quite small (10-20%), although cis-1,2-dichloroethene episulfide was the major component (80%) of the products. This necessarily suggests that k_b and M_{kd} are small and that k_j is large. The fact that cis-1,2-dichloroethene episulfide is the major product of this reaction, must mean that k_e (rotation) is also small.

Stereospecificity of the addition of $S(^3P)$ atoms to cis and trans-1,2-dichloroethylenes.

The earlier proposed concept that the stereospecific addition of a divalent species is dependent on the spin state of the species is invalid in the case of $S(^3P)$ addition, as indicated by the apparent stereospecific addition of this triplet species. Retention of configuration is observed for both isomeric forms of 2-butene (26), 1,2-difluoroethylene (70), and 1,2-dichloroethylene.

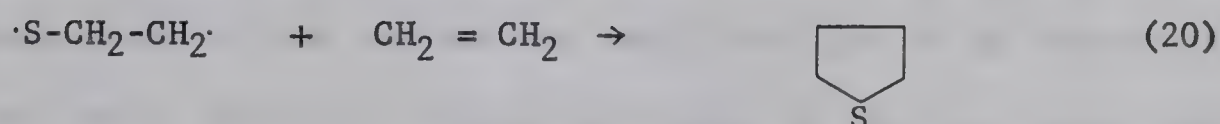
Skell and Woodworth (20) put forward initially, the concept that stereospecific addition of singlet methylene resulted from an insertion into the π bond of the olefin via a three-center mechanism with simultaneous bond formation to both of the olefinic carbon atoms. Furthermore it was suggested that triplet addition resulted

in formation of an initial triplet biradical in which rotation about the C-C bond has a low energy barrier. Spin inversion was believed to be much slower than rotation thus accounting for the apparent non-stereospecific addition of triplet methylene.

Benson and DeMore (7) are of the opinion that the detailed mechanism must include formation of a short-lived biradical as the initial step for both singlet and triplet methylene addition. The degree of stereospecificity is then determined by the rate of ring closure vs. the rate of rotation about the C-C bond. They calculated that for a trimethylene biradical containing 32.7 kcal./mole excess energy (triplet addition), ring closure is faster than rotation by a factor of $10^{0.8}$. Singlet addition, due to the larger excess energy in the biradical, should exhibit even faster ring closure. These authors feel that there is as yet no convincing evidence that addition of triplet CH_2 to olefins is less stereospecific than addition of singlet CH_2 . Gaspar and Hammond (16) disagree with Benson and DeMore claiming that even with a highly excited trimethylene biradical the rate of rotation should at least equal the rate of cyclisation. As relaxation of the radical occurred the rate of rotation should exceed the rate of cyclisation. They estimate that the barrier to rotation should not exceed 3 kcal./mole thus making the rotation a very favorable process. Gaspar and Hammond believe that stereospecific addition demands simultaneous formation of two bonds.

The stereospecific addition of $\text{S}(^3\text{P})$ atoms must favor the hypothesis of Benson and DeMore in that a competition between ring closure and rotation about the C-C bond determines the products resulting from the initial triplet biradical. Ring closure in the case

of thiodimethylene biradicals ($\cdot\text{SCH}_2\text{CH}_2\cdot$) has been shown to be a rather slow process. Photolysis of ethylene episulfide in the presence of ethylene was found to yield small amounts of tetrahydrothiophene (26).



The most obvious reaction to account for the tetrahydrothiophene formation would be addition of thiodimethylene biradicals to ethylene. A similar addition of $\cdot\text{S}-\text{CH}_2-\text{CH}_2\cdot$ to acetylene was observed.

From the Rice-Ramsperger-Kassel relation

$$k = A(E-E_a/E)^{s-1} \quad (21)$$

the low exothermicity of the addition reaction (E probably less than 10 kcal./mole) together with a ring strain for thiacyclopropane of 9 kcal./mole (81) (resulting in a high E_a) indicates a low value for the rate constant for ring closure.

The above arguments strongly suggest that thiodimethylene biradicals have a long lifetime, and therefore the observed stereospecificity of the $\text{S}(^3\text{P})$ addition cannot be due to the facile nature of ring closure, but rather to the slow rate of rotation.

The slow rate of rotation may be due in part to the heavier sulfur atom, as compared to CH_2 or the O atom, where non-stereospecific addition of these latter species in their triplet states was observed.

A barrier to rotation may also arise from the interaction of the vacant d orbital of the sulfur atom with the p electron on the carbon atom. This effect would not be possible for CH_2 and O atom since d orbitals are not available for these species.

The apparent large barrier to rotation also suggests that the unpaired electrons on the initial triplet biradical are not completely independent of one another and that there may be an interaction between the two p orbitals. Benson and DeMore as well as Gaspar and Hammond treat the trimethylene biradical as two independent doublets with no interaction between the two unpaired electrons. They estimated the potential barrier to rotation to be about 3 kcal/mole.

Crawford and Mishra have recently studied the pyrolysis of a series of 1-pyrazolines and have established that expulsion of N_2 results in the formation of trimethylene biradicals, (82). The nature of the products, however, indicate that the two terminal carbons are influenced by each other and calculations have been made to estimate the strength of the influence. The calculations indicate that the interaction of the p electrons does not allow the 'biradical' to be a pair of freely acting radicals and further suggests a bonding energy of 8-12 kcal/mole. It has been suggested that due to the proximity of the two carbon atoms, $\text{P}\pi\text{-P}\pi$ bonding occurs, forming the species, π -cyclopropane.

Hoffmann (83), from extended Huckel M. O. calculations, suggests that addition of CH_2 ^1A to ethylene results in formation of a singlet biradical. Calculations of the potential surface of the trimethylene system indicate that collapse of the biradical to cyclopropane faces increasing barriers to rotation of the terminal CH_2 groups.

Although the spin state of the trimethylene will influence the lifetime of the biradical Hoffmann feels that stereospecific addition is due to rotational barriers, caused by spin interaction, rather than to rapid ring closure of the singlet biradical.

Calculations on the trimethylene biradical formed by addition of triplet methylene to ethylene show no rotational barriers but a freely rotating complex. This is consistent with the non-stereospecific addition of triplet CH_2 to olefins.

Due to the large size of the sulfur atom, triplet addition to the double bond, unlike triplet methylene addition, may result in a larger spin interaction of the two unpaired electrons thus resulting in a rotational barrier. An additional barrier to rotation may result from steric effects involved in rotation about the C-C bond. This potential energy barrier may be greater than the 3 kcal/mole estimated for trimethylene.

The total barrier to rotation for the triplet sulfur biradical may be greater than 10 kcal/mole. Addition of $\text{S}(^3\text{P})$ to the double bond is exothermic by ca. 10 kcal/mole or less. This low exothermicity of the addition reaction may therefore be insufficient to overcome the rotational barrier and probably constitutes the major reason for the stereospecific addition of $\text{S}(^3\text{P})$ atoms to olefins.

C. REACTIONS OF SULFUR ATOMS WITH CHLORO ALKANES

Results

1. Methyl chloride

A. Static System

The photolysis of carbonyl sulfide with methyl chloride in low conversion runs, did not result in the production of any volatile sulfur-containing compounds. The only product of the reaction observed, other than CO, was a dark yellow solid deposited on the walls of the reaction vessel. The yield of carbon monoxide is shown as a function of methyl chloride pressure in Table XV and Figure 26. The rate of CO formation drops very slowly and at a pressure of 460 torr methyl chloride (methyl chloride/COS ratio = 4.6) the rate of CO formation has dropped only by 23% of the value obtained when no halide is present. This would correspond to a consumption of 46% of the initially produced sulfur atoms. The production of CO at this point is still far above the $R^0(\text{CO})/2$ value and from Figure 26 it can be seen that a pressure of methyl chloride far above 1000 torr would be needed to bring $R(\text{CO})$ to a value of $R^0(\text{CO})/2$.

B. Flash photolysis-kinetic mass spectrometry

A mixture of COS (400 microns) and methyl chloride (800 microns) was flashed and a signal at mass 82 was obtained. This signal, shown in Figure 27, corresponds to a CH_3ClS product. Although the signal contained a considerable amount of background noise it showed a definite decrease with time indicating that the product producing it was not stable. This result is consistent with the lack of a CH_3ClS product in the static system.

TABLE XV
VARIATION OF PRODUCT DISTRIBUTION AS A FUNCTION OF
METHYL CHLORIDE PRESSURE IN THE
COS - METHYL CHLORIDE SYSTEM^a

P(CH ₃ Cl) torr	Rates, μ moles/30 min.	
	CO	Volatile Product
0	9.60	none
24.3	9.46	-
53.4	8.82	-
104.0	8.42	-
202.5	8.20	-
304.1	7.85	-
460.6	7.36	-

^a P(COS) = 100 torr,

Irradiation time = 30.0 min.

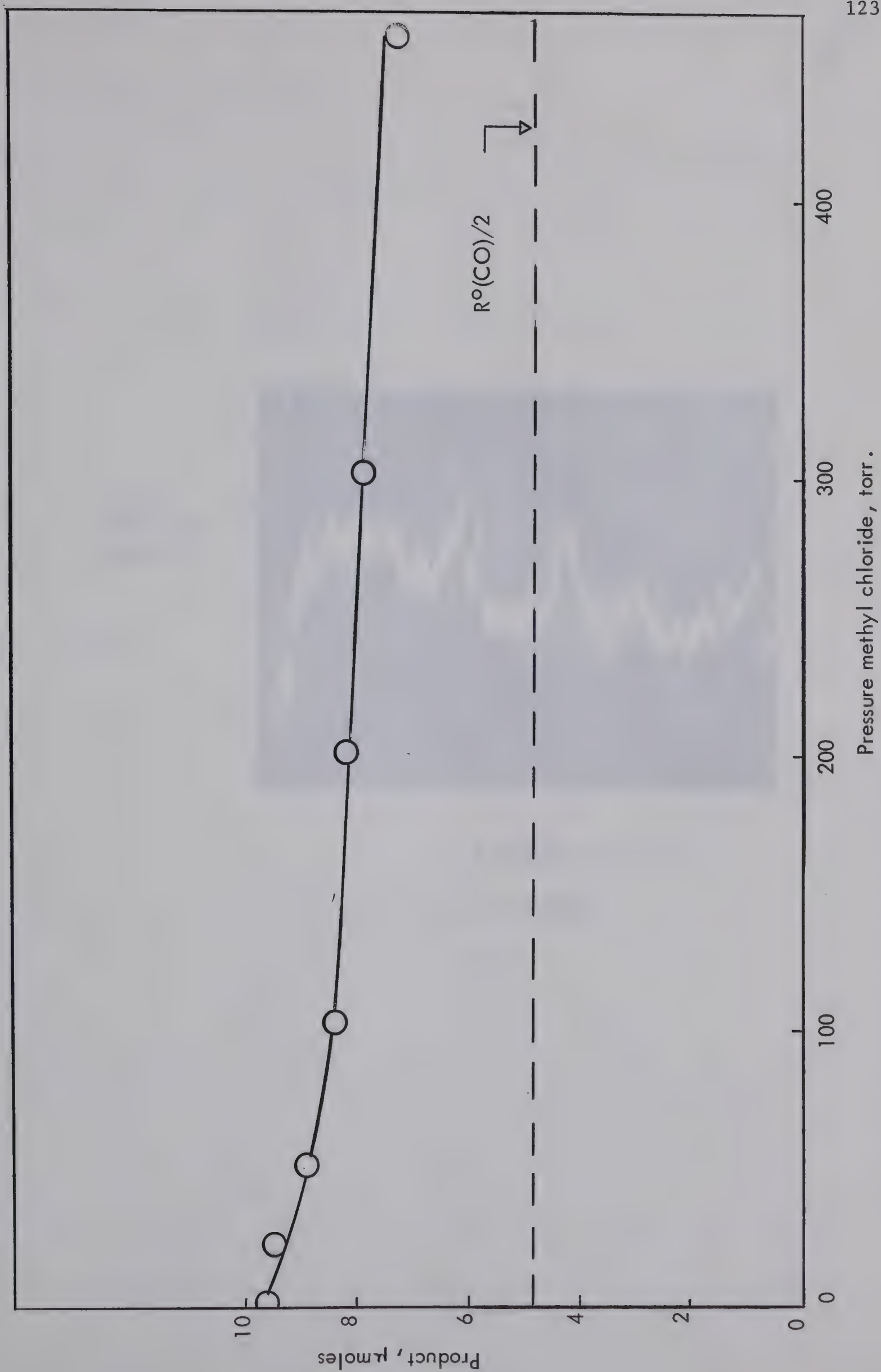
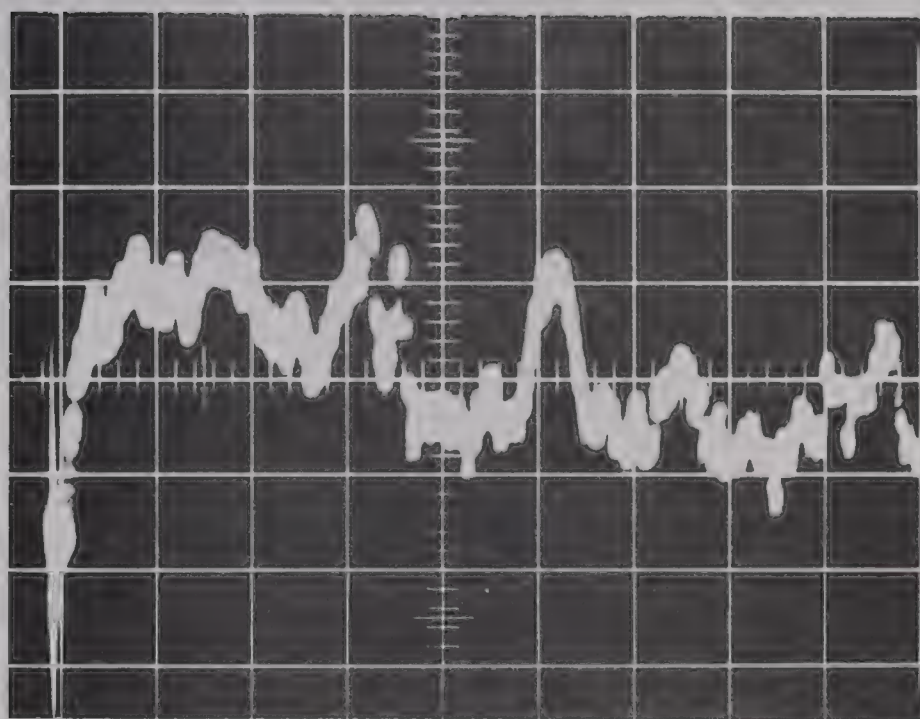


Fig. 26 CO production as a function of methyl chloride pressure.

50.0
Millivolts
per div.



10.0 Milliseconds per div.

Fig. 27 Mass 82, CH_3ClS

2. Chlorodifluoromethane

Photolysis of carbonyl sulfide with chlorodifluoromethane resulted in observations similar to those found for methyl chloride. No volatile product other than CO was found and, unlike methyl chloride, no solid other than elemental sulfur was formed in the reaction.

The rate of CO formation vs. substrate pressure is shown in Table XVI and Figure 28 and is seen to decrease with pressure even more slowly than in the case of methyl chloride. At a ratio of chlorodifluoromethane/COS = 5.0 the R(CO) value has dropped only by ca. 17%. No products other than those found in the photolysis of pure COS were found in this reaction.

Ethyl Chloride

The photolysis of ethyl chloride with COS produced two sulfur containing products with relative retention times of 1.00 (I) : 10.00 (II) on a 4 ft. T.C.P. column. Product I was identified by mass spectrometry and by comparison of its G.C. retention time with an authentic sample to be ethylene episulfide. The second sulfur containing compound was identified as 2-chloroethyl mercaptan. This product was identified by comparing its G.C. retention time with that of an authentic sample. The sample of 2-chloroethyl mercaptan was synthesized by photolysis of a mixture of H₂S and vinyl chloride. The reaction proceeds mainly by terminal addition of HS to vinyl chloride,

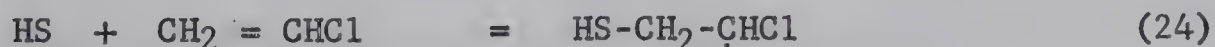
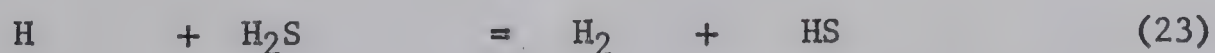


TABLE XVI
VARIATION IN PRODUCT YIELD AS A FUNCTION OF
CF₂HCl PRESSURE IN THE COS - CHLORODIFLUOROMETHANE SYSTEM^a

P(CF ₂ HCl torr)	Results, μ moles/30 min.	
	CO	Volatile Product
0	7.26	none
48.5	6.94	-
156.6	6.54	-
510.5	6.00	-

^a P(COS) = 100 torr,
irradiation time = 30.0 min.

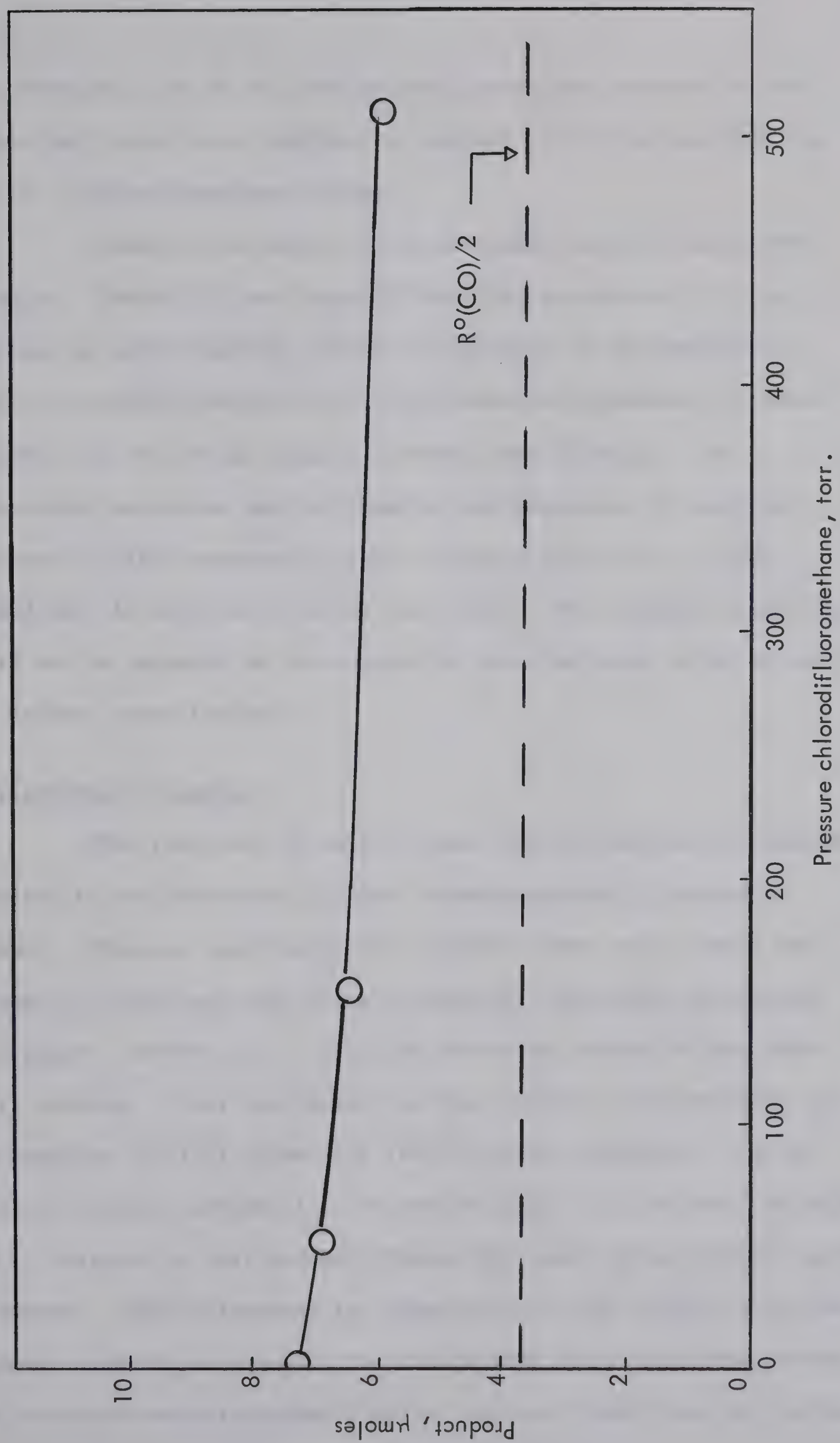


Fig. 28 CO formation as a function of chlorodifluoromethane pressure.

The retention time of the 2-chloroethyl mercaptan produced in this manner was found to be identical to product II of this reaction, on a 4 ft. tricresylphosphate column.

Quantitative analysis was performed only for the carbon monoxide. Table XVII and Figure 29 show the production of CO as a function of ethyl chloride pressure. The rate of CO formation is seen to drop quite rapidly and at high substrate pressures it seems to level off at a value slightly greater than $R^O(\text{CO})/2$. The 2-chloroethyl mercaptan was not found at low pressures of substrate and even at high pressures of ethyl chloride (1000 torr) it was formed only in very small yields (ca. 2-3%). The ethylene episulfide could not be measured as its separation from the ethyl chloride could not be done quantitatively.

Tertiary-Butyl Chloride

The reactions of sulfur atoms with tertiary-butyl chloride resulted in the formation of a gas chromatographically separable product. The mass spectrum of this product shows only a small peak at mass 124, the next peak being at mass 88. Mass 124, corresponds to a $\text{C}_4\text{H}_9\text{SCl}$ product, i.e., a sulfur insertion product of tertiary-butyl chloride. Only two isomers of this product are reasonable for the reaction of $\text{S}(^1\text{D})$ atoms with tertiary-butyl chloride. They are 2-chloro-2-methyl-propane-1-thiol and tertiary-butyl sulfenyl chloride. N.M.R. analysis of this product (Figure 30) shows three distinct groups of protons. This eliminates the possibility of the product being the sulfenyl chloride as its spectrum should show nine equivalent protons. The 2-chloro-2-methyl-propane-1-thiol does have three types of protons

TABLE XVII

VARIATION IN PRODUCT YIELDS AS A FUNCTION OF ETHYL
CHLORIDE PRESSURE IN THE COS - ETHYL CHLORIDE SYSTEM^a

P(C ₂ H ₅ Cl) torr	Result, μ moles/30.0 min.			Ethylene episulfide
	CO	HS-CH ₂ CH ₂ Cl		
0	7.26	None		not measured
51.1	5.86	-		
99.9	5.18	-		
206.7	4.79	-		
405.6	4.34	-		
702.7	4.36	Trace		
1010	4.00	Trace		

^a P(COS) = 100 torr,

Irradiation time = 30.0 min.

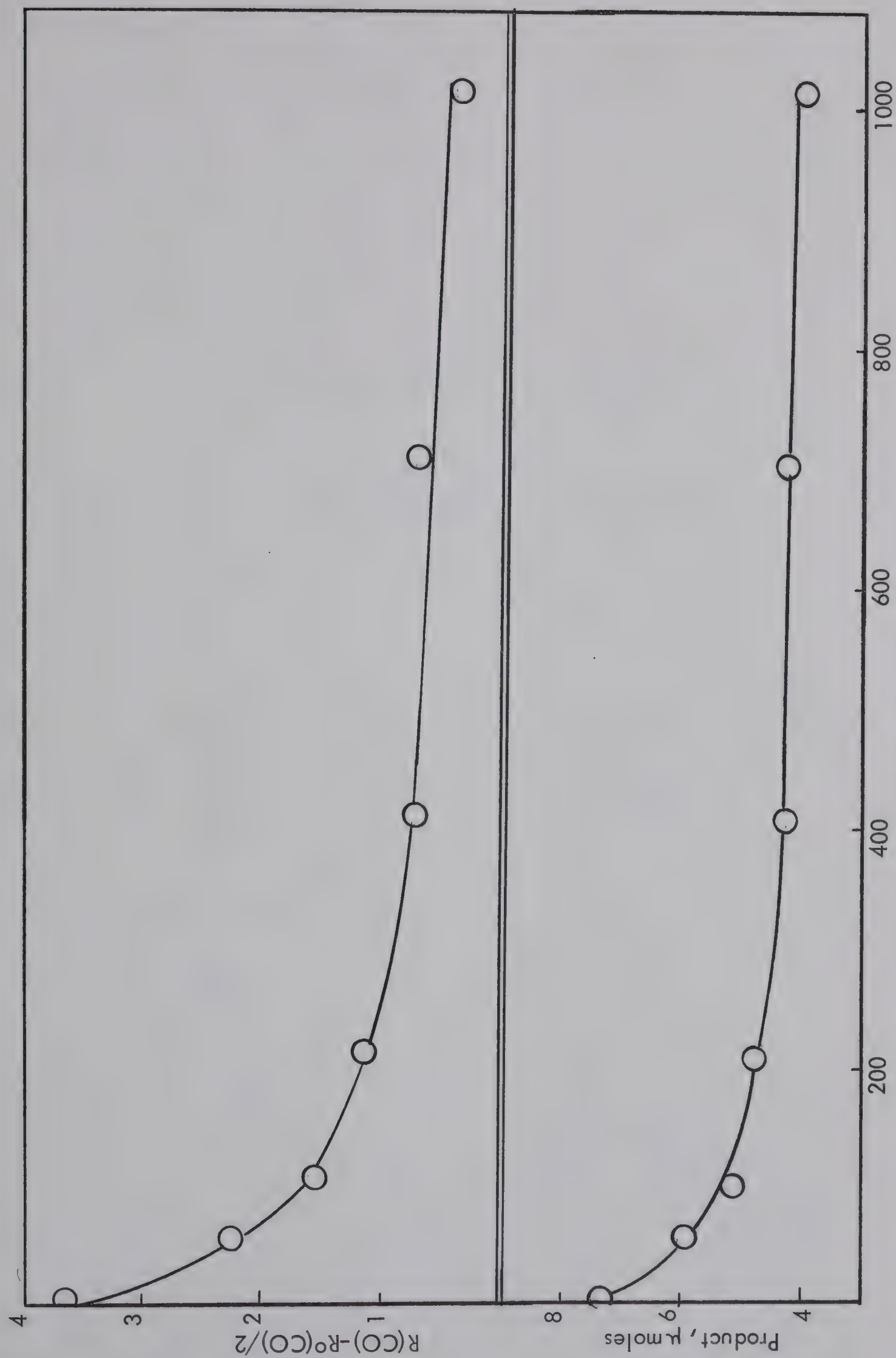


Fig. 29 $R(CO) - R_0(CO)/2$ and CO formation as a function of ethyl chloride pressure.

N. M. R.

2-CHLORO-2-METHYL-PROPANE-1-THIOL

Assignments (τ)

- a. 7.13, 7.22
- b. 8.35
- c. 8.51, 8.58, 8.63, and 8.70

Relative intensities, a:b:c: = 2:7:1.9

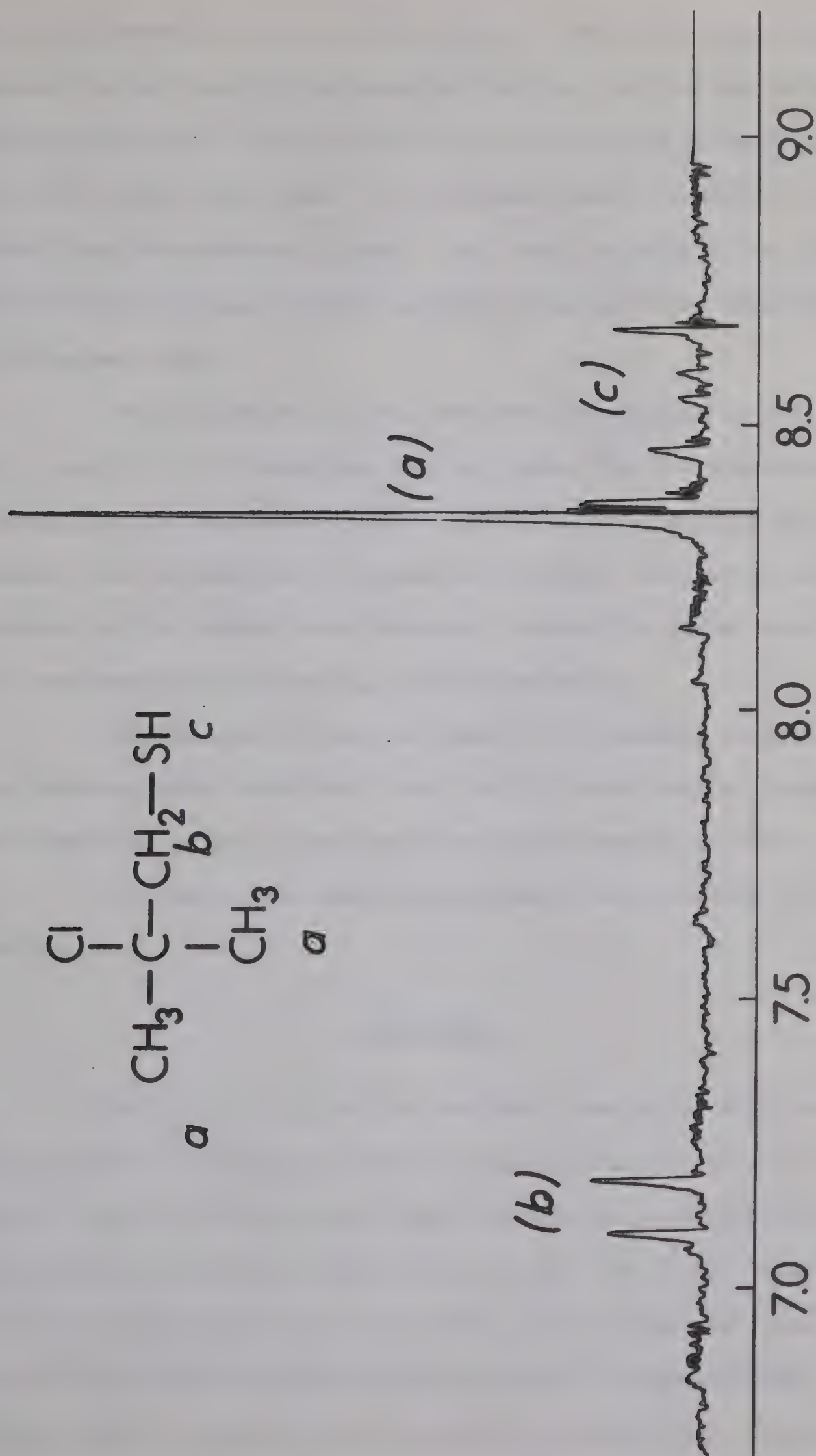


Fig. 30 Nuclear Magnetic Resonances Spectrum of 2-chloro-2-methylpropane-1-thiol.

and is believed to be the reaction product. The N.M.R. spectrum, however, is not exactly that expected for the β -chloro mercaptan. Although the methyl and methylene protons seem to be properly assigned with the proper intensities, the S-H proton shows a quartet splitting rather than the expected triplet. The close proximity of the chlorine atom to the SH group, however, may affect the splitting thus giving the observed signal.

It is important to note here that the product is definitely not a result of C-Cl insertion but must arise from C-H insertion. This argument is also supported by the cracking pattern observed for the product. HCl elimination is common for β -chloro mercaptans and alcohols and the highest mass observed, besides the parent peak of 124, was mass 88 corresponding to HCl elimination.

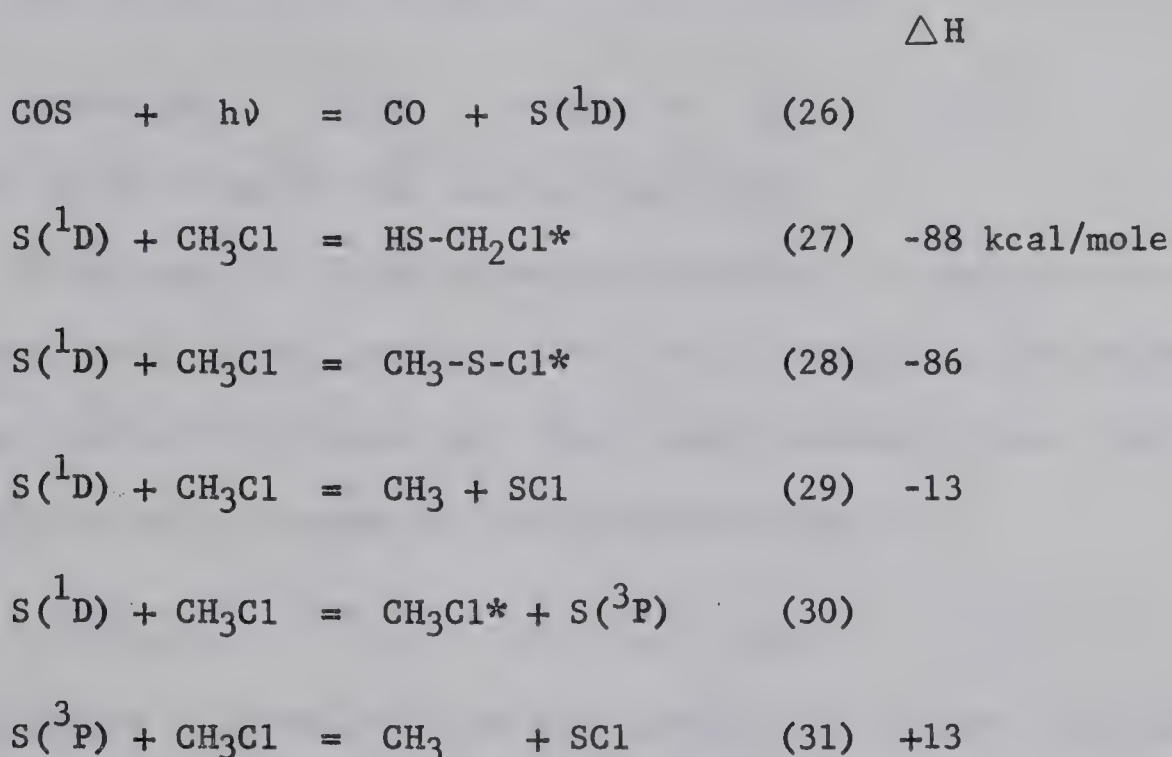
The reaction product was found to be unstable towards the gas chromatographic conditions used, and its decomposition product was identified by mass spectrometry as isobutylene episulfide.

No other sulfur containing products were observed in this reaction.

DISCUSSION

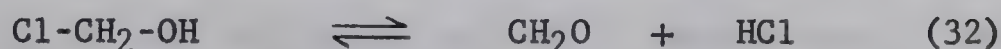
The initial step in the reaction of methylene with mono-chloroalkanes in the liquid phase has been reported to be a C-Cl insertion, (84, 85) while recent studies of the gas phase reaction of methylene with methyl chloride have shown that the initial reaction proceeds mainly by Cl abstraction (86). Carbon atoms have also been shown to insert into carbon-chlorine bonds of chlorinated hydrocarbons (112). Studies of the reactions of sulfur atoms, carbon atoms

and methylene have conclusively shown that these biradicals, in their singlet states, insert into C-H bonds. It is reasonable then to consider that the reaction of sulfur atoms with methyl chloride may proceed by C-H insertion, C-Cl insertion and/or Cl abstraction. The following reactions can be written in considering the above possibilities.

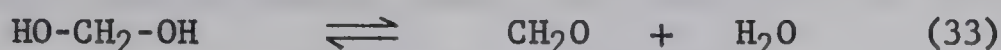


The ΔH of each reaction, calculated from bond energies, is also shown. The feasibility of each of these initial reactions is now considered in light of the experimental observations. Step 27 deserves first consideration in view of the reactions observed between $\text{S}({}^1\text{D})$ atoms and paraffins. Insertion of the sulfur atom into the C-H bond would produce a hot chloromethyl mercaptan having an excess energy of 88 kcal/mole. This product has not been reported in the literature and present knowledge of analogous compounds would indicate that chloromethyl mercaptan is not a stable compound at room temperature.

Among analogous oxygen compounds, chloromethyl alcohol has been reported to exist only in equilibrium with formaldehyde and hydrogen chloride (87).

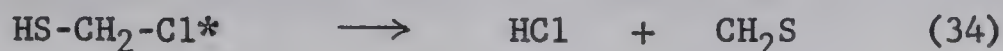


Attempts at isolating the chloro alcohol have not been successful. This is also true in the case of dihydroxy methane. This compound exists only in an aqueous solution of formaldehyde,



and cannot be isolated as the pure product (88).

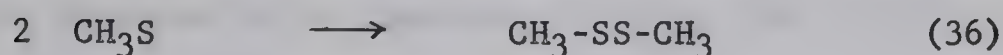
Returning now to chloromethyl mercaptan, it must be concluded that, even if this product were fairly stable at room temperature, the initially produced hot adduct would probably have a very short lifetime and decompose by the following method.



Thioformaldehyde is known to trimerise immediately to give trithiane, a non-volatile solid, which may account for the solid formed in this reaction. The HCl would remain undetected as it is impossible to separate this product from the large excess of COS used in the reaction. Decomposition of the hot mercaptan by C-S and/or H-S bond rupture, as was observed in the $\text{S}(^1\text{D})$ - methane system, does not occur here since products due to the fragments $\cdot\text{CH}_2\text{Cl}$ and $\cdot\text{SCH}_2\text{Cl}$ were not observed.

Insertion of the $\text{S}(^1\text{D})$ atom into the C-Cl bond would result in the formation of a hot methyl sulfenyl chloride, the reaction being 86 kcal/mole exothermic. Methyl sulfenyl chloride has been prepared and is described as a fuming orange liquid, very sensitive to heat and light (89). The chlorine atom of sulfenyl chlorides has been

described as extremely active and these compounds are known to add across olefinic double bonds in a dark reaction. They have also been reported to undergo visible photolysis in which the primary step is the cleavage of the S-Cl bond (90, 91). This strongly indicates that if C-Cl insertion occurs in this system, isolation of a stable sulfenyl chloride product would be essentially impossible. The product, if formed, would probably undergo S-Cl bond rupture and the recombination of CH_3S radicals should result in formation of a stable and easily detectable product, dimethyldisulfide.

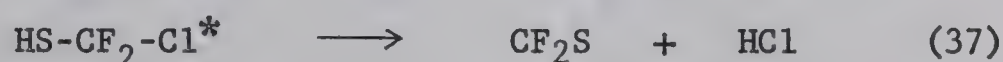


This product was not produced in this reaction and it can be assumed with considerable certainty that C-Cl insertion does not occur in this system.

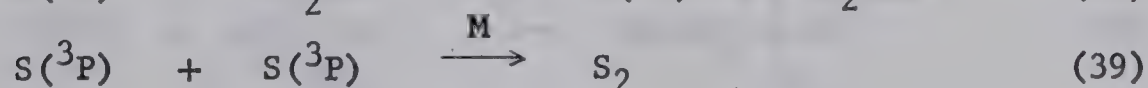
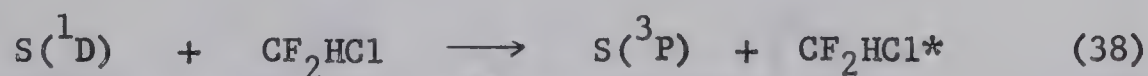
Reactions 29 and 31, (i.e., abstraction of Cl), are also eliminated since no ethane was found in this reaction.

Of all the reactions considered the only one compatible with the observations is step 27 followed by decomposition of the hot mercaptan to thioformaldehyde and HCl. The rate of insertion of sulfur atoms into C-H bonds of methane was found to be much slower than that for ethane or other paraffins. The slow rate of CO decrease, in the methyl chloride system, is in accordance with this observation, although the relative inertness of methyl chloride may be due to an increased efficiency for deactivating $\text{S}(^1\text{D})$ atoms to $\text{S}(^3\text{P})$, due to the substrate molecule possessing a large chlorine atom.

The inability to identify conclusively any of the reaction products, however, must necessarily leave some doubt as to the primary reaction of $S(^1D)$ atoms with methyl chloride. In an attempt to test the possibility of reaction 27, the photolysis of COS was carried out in the presence of chlorodifluoromethane. If insertion into the C-H bond occurred the hot mercaptan would be expected to decompose in the following manner.



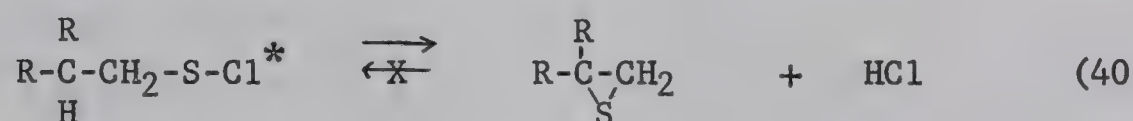
Since CF_2S is a relatively stable product, dimerising only slowly, it could be detected as a reaction product. The results of this reaction, however, show that chlorodifluoromethane is an inert substance. The only products formed were CO and elemental sulfur, products of the photolysis of pure COS. The presence of two fluorine atoms and one chlorine atom on the molecule appear to render the molecule inert towards reaction. The slow decrease in the rate of CO formation is due to deactivation of $S(^1D)$ to the ground state and increased recombination of $S(^3P)$ atoms.



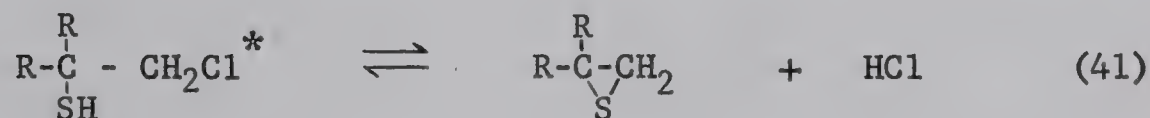
The reactions of sulfur atoms with higher alkyl chlorides continue to show a lack of C-Cl insertion while indicating that C-H insertion is the only primary reaction. The same arguments used for methyl chloride can be used here to suggest that C-Cl insertion does not occur: with ethyl chloride and tertiary-butyl chloride no

sulfenyl chlorides or decomposition products, such as disulfides, were observed.

One further possibility cannot be overlooked. Although sulfenyl chlorides are known to react by S-Cl bond split, HCl elimination could also be a possible decomposition path:

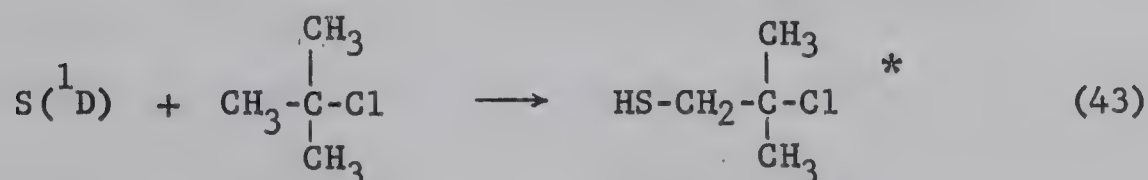
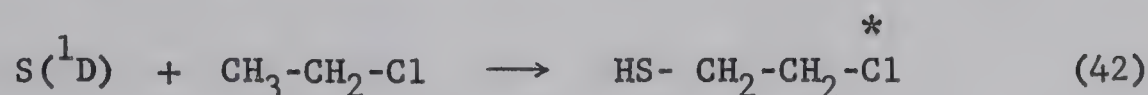


This reaction, however, unlike the decomposition of chloro mercaptans,

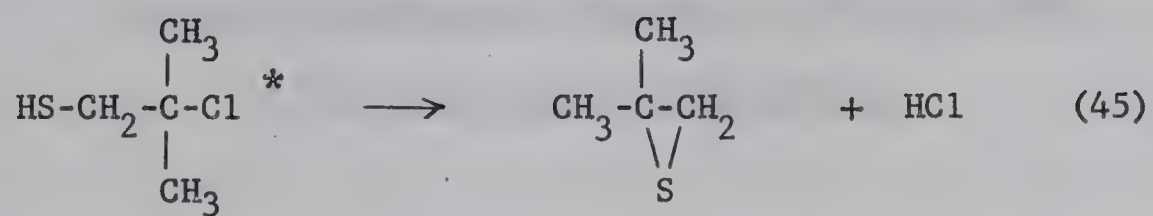
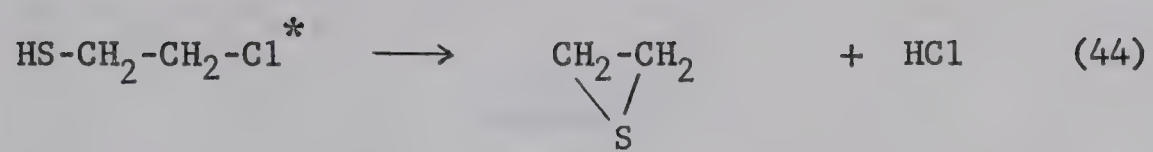


does not exhibit reversibility. (113, 93)

Insertion of S(¹D) atoms into C-H bonds of alkyl chlorides is conclusively indicated from the reaction products observed with ethyl chloride and tertiary-butyl chloride:



Both of these products have been identified in these reactions although they are produced in relatively small yields. The main fate of the initially produced hot β-chloro mercaptans is decomposition to HCl and the corresponding episulfide.



CHAPTER V

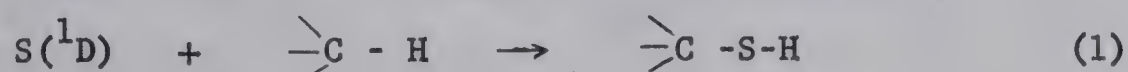
TRANSITION COMPLEXES INVOLVED IN THE REACTIONS OF SULFUR ATOMS WITH OLEFINS

A. Reaction With Alkenyl C-H Bonds

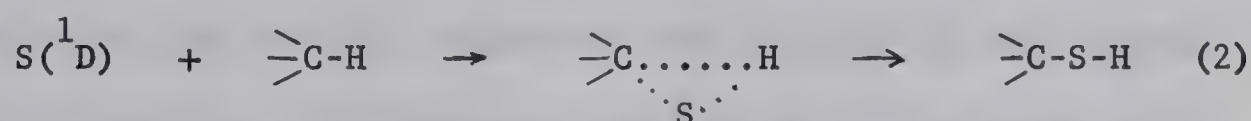
Addition of a large excess of CO_2 was shown to diminish the formation of mercaptans in the reaction of sulfur atoms with olefins. This effect is due to the efficient electronic relaxation of the $\text{S}(^1\text{D})$ atom to the $\text{S}(^3\text{P})$ state brought about by the CO_2 . That the CO_2 does not inhibit mercaptan formation by some process of pressure stabilization of the initial products is indicated by the lack of such a pressure effect in the COS-cyclopentene system (Fig. 7). These results therefore indicate that alkenyl mercaptans are formed from $\text{S}(^1\text{D})$ atom precursors alone and that $\text{S}(^3\text{P})$ atoms are inert towards the C-H bond.

The reaction of $\text{S}(^1\text{D})$ with the C-H bonds in olefins produced only one type of product; the corresponding mercaptan. No other products such as those which would be formed by recombination or disproportionation of alkyl radicals, were formed. The presence of HS radicals was not indicated (i.e., no hydrogen abstraction). These results clearly show that $\text{S}(^1\text{D})$ atoms react with the C-H bond in one step without the formation of intermediate radicals.

This reaction can only be described as an insertion type reaction:

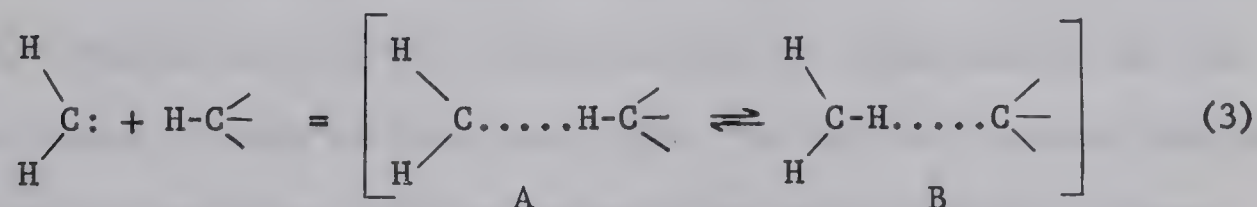


Little is as yet understood concerning the transition state involved in the insertion process. As no free radical intermediates are involved in the reaction, such as insertion process would suggest simultaneous formation of C-S and S-H bonds with a simultaneous breaking of the C-H bond. The transition state may be described as a three-membered cyclic complex formed by insertion of $S(^1D)$ into the C-H bond.

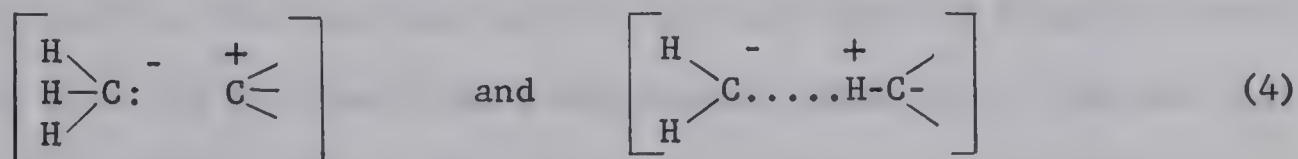


A one-step direct insertion described by a triangular transition state was earlier proposed for methylene insertion into C-H bonds (92).

Recently DeMore and Benson (7) suggested that, for CH_2 reactions, insertion is best explained by attack of the CH_2 on the H atom rather than on the electrons of the double bond.



Adduct B is equivalent to the recombination complex of radicals $CH_3\cdot$ and $\cdot C\equiv$. Bond formation could be accomplished simply by rotation of the radicals into a position favoring orbital overlap. The attractive potential between the loosely associated radicals is ascribed to partial contribution of ionic states such as:



This mechanism, however, does not distinguish between the electronic states of methylene and would suggest that insertion and abstraction depend only on the energetics of the reaction. The higher the energy content of the methylene the greater should be the probability that adduct B will fall apart into radicals. This is contrary to experimental results where the higher energy singlet CH_2 shows insertion while the lower energy triplet CH_2 shows only abstraction (115). Ring and Rabinovitch have recently suggested that triplet CH_2 may undergo an insertion reaction (116), however this has not as yet been conclusively shown.

The above type of mechanism, proposed by DeMore and Benson, cannot explain the results of reactions of oxygen atoms with paraffins. Yamazaki and Cvetanovic (50) have shown that $\text{O}(^1\text{D})$ atoms insert indiscriminately into C-H bonds while $\text{O}(^3\text{P})$ atoms, having 46 kcal/mole less energy, are found to only abstract. Insertion of $\text{O}(^3\text{P})$ atoms into C-H bonds would be only slightly more exothermic than $\text{S}(^1\text{D})$ atom insertion. Therefore if $\text{O}(^3\text{P})$ insertion occurs, stabilization of the insertion product should be observed. This is contrary to experimental evidence which shows that triplet oxygen atoms only abstract H atoms from paraffins.

There is as yet no convincing evidence that triplet species are capable of undergoing insertion reactions. On the other hand there is no doubt that singlet species insert indiscriminately into C-H bonds. The insertion reaction is, therefore, a characteristic of the spin state of the reacting species and must involve a spin-allowed insertion into the C-H bond with simultaneous formation of the two new bonds and breaking of the C-H bond.

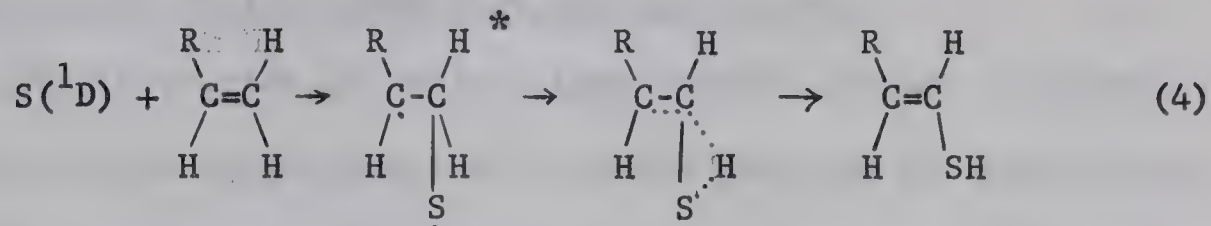
B. Reaction with Vinylic C-H Bonds

Unlike the indiscriminate insertion of $S(^1D)$ atoms into alkenyl C-H bonds the reaction of $S(^1D)$ atoms with vinylic C-H bonds definitely favors formation of terminal vinylic mercaptans. No measurable non-terminal vinylic mercaptans are formed with propylene (71), 1-butene or cis and trans-2-butenes (26), while terminal vinylic mercaptans are formed in essentially statistical amounts. The present work also shows that non-terminal vinylic mercaptans are minor products; the yield of cyclopentene-1-thiol being ca. 5% for cyclopentene and only trace amounts of cyclohexene-1-thiol are formed in the cyclohexene case. This latter result is contrasted with the reaction of methylene with cyclohexene where the product yields were found to be: norcaradiene 40%, 3-methyl cyclohexene 25%, 4-methylcyclohexene 25% and 1-methyl cyclohexene 10% (18).

A fact which is immediately evident from the data is that vinylic mercaptans are formed only when the carbon atom on the double bond is bonded to two hydrogen atoms. This may lead one to suggest that two carbon-hydrogen bonds are participating in the reaction complex. This idea is, however, quickly dispelled when one considers that random insertion is observed for the tertiary C-H bond of isobutane (72).

The large reactivity of the terminal part of the double bond, however, does suggest an orientation effect such as is observed for radical additions to the double bond. For this orientation effect to occur, however, the primary reaction must be with the carbon center of the double bond and not with the C-H bond. This then-

necessitates that mercaptan formation arises from isomerisation of the initially formed singlet biradical:



Thermodynamically the isomerisation process should be possible. The exothermicity of the above reaction is about the same as that for addition of triplet oxygen atoms. Yet in the latter case extensive isomerisation and internal hydrogen migration as well as fragmentation occur. With the oxygen atom adduct the hydrogen migration has been suggested to be from one carbon atom to another (53), resulting in the aldehyde product. There seems to be no significant reason why hydrogen migration could not take place from the carbon atom to the oxygen atom resulting in a vinylic alcohol, which, owing to its inherent instability, would isomerise giving the required aldehyde. In the sulfur atom case the thiol is more stable than the aldehyde and the reaction would be stopped at the vinylic mercaptan stage.

Although this argument is consistent with the results for olefins having terminal CH_2 groups, it does not explain the lack of vinylic mercaptan formation with the 2-butenes, cyclopentene and cyclohexene. Here addition to either end of the double bond should yield non-terminal vinylic mercaptans due to the symmetry of the molecules. This problem can be resolved only by suggesting that energy dissipation from the reaction site is faster in the case of non-terminal addition than in terminal addition. If this is

so terminal addition will favor isomerisation while non-terminal addition will favor ring closure to the episulfide.

C. Reactivity of Sulfur Atoms With the Double Bond

The reactivity of sulfur atoms towards olefins is clearly suggestive of spin state reactions in which the type of reaction depends on the spin state of the atom. It is not unreasonable then to consider that the reactivity of $S(^1D)$ and $S(^3P)$ atoms may differ with respect to addition to the double bond. Before discussing possible transition complexes for the addition reaction it seems necessary first to review the existing literature on such addition reactions and later to compare these systems to the sulfur atom system.

Extensive studies of the addition of radical reagents such as H , CH_3 and CCl_3 radicals to various aromatic, olefinic and acetylenic compounds have been carried out. The results show how the rate constants of addition depend on the atom localisation energies of the substrate and the steric hindrance caused by the presence of bulky groups attached to the reaction center. The atom localisation energy is defined as the energy required to localise a π electron on a particular carbon atom of a double bond.

Jennings and Cvetanovic (94) observed that the rate of hydrogen atom addition to olefins did not vary much with alkyl substitution on the double bond. Although a correlation with electron density of the double bond was not obtained a good correlation of log relative rate constant vs. localisation energy was observed. This indicates that reactivity is related to a particular reaction center rather than to the double bond as a whole.

Szwarc (95) reported a linear relationship between the logarithms of the methyl affinities and localisation energies for a series of aromatic compounds. Singlet-triplet excitation energies of the aromatic compounds were also found to correlate well with the observed methyl affinities. Singlet-triplet excitation energies are linearly related to the localisation energies as they both involve localisation of a π electron on the carbon atom.

Coulson (96) found a good linear correlation of the logarithms of the rate constants of methyl addition with free valences and localisation energies, the last two quantities being linearly related between themselves for these hydrocarbons.

That mono radical addition involves a specific carbon center was clearly illustrated by the effects of substituting a methyl group for a H atom on a reactive center. The relative rate constants for methyl radical addition to 1,3-butadiene and 2,3-dimethyl-1,3-butadiene are 2090 and 2200 respectively while a decrease to 300 is observed for 1,4-dimethyl-1,3-butadiene (97). This indicates clearly that the positions 1 and 4 of butadiene are by far the most reactive.

From Table XVIII it can be seen that although the reactivity of H atoms correlates well with localisation energies, for CH_3 radicals cis and trans-2-butenes show a much lower reactivity than would be predicted from localisation energies. This must necessarily indicate a steric hindrance due to the methyl substituent on the double bond. A similar 'blocking' technique has been employed for elucidating the reactive carbon centers of large aromatic compounds (98).

TABLE XVIII
RELATIVE REACTIVITY OF RADICAL REAGENTS
WITH A SERIES OF OLEFINS

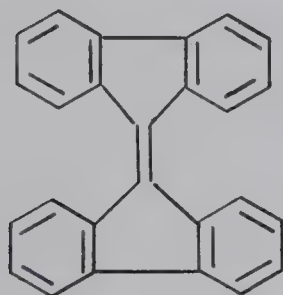
Olefin	H ^a	CH ₃ ^b	Localisation energy ^c
ethylene	1.0	1.0	1.5822
ethylene-F ₄	-	10.0	-
propylene	1.8	1.3	1.5336
1-butene	1.9	1.6	1.5301
iso-butene	4.4	2.1	1.4854
<u>cis-2-</u> butene	0.85	0.08	1.5658
<u>trans-2</u> butene	1.1	0.15	1.5658

a. Ref. (94)

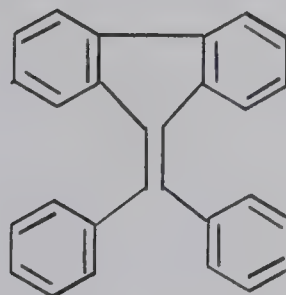
b. Ref. (101)

c. Ref. (103)

The calculation of localisation energies involves the exchange integral β which depends on the extent of overlap of the two adjacent p orbitals of the double bond. Changes in the exchange integral therefore should lead to corresponding changes in the methyl affinities. This effect is demonstrated by observing the reactivities of dibisphenylene ethylene A and diphenyl-bisphenylene ethylene B (95).



A rel. $k = 1370$



B rel. $k = 15$

The twisting of a double bond results in decreased overlap of the p electrons therefore resulting in a lowering of the localisation energy. Compound A contains a twisted double bond while in compound B free rotation along the C-Ph bonds makes it possible to avoid such twisting. Szwarc has also observed that a stretched double bond results in greater reactivity than a normal double bond (95).

The blocking effect of methyl substituents as well as the general treatment based on the concept of localisation energy prove that the transition state in the radical addition reaction involves a particular carbon center and not the π -electron system as a whole.

Szwarc (95) has proposed an energy diagram to illustrate many of the observations of radical addition to the double bond.

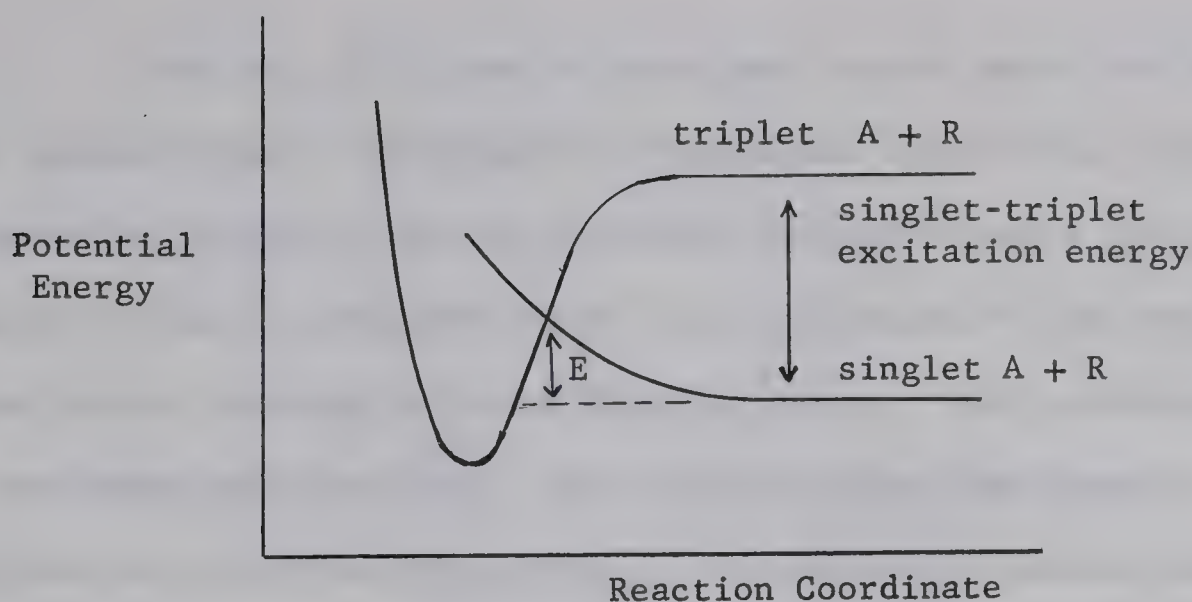


Fig. 31. A potential energy - reaction coordinate diagram for reaction of radicals with olefins.

The existence of an activation energy in a reaction implies that some repulsive forces participate in the interaction involving the reaction partners. In the case of a radical this repulsive force is a coulombic force between the negative π -electron cloud of the olefin and the p electron of the radical. On the other hand a triplet state of the olefin (electrons localised on the carbon atoms) attracts a radical and the potential energy curve resembles that of a Morse curve. For a similar series of olefins reacting with the same R the shape of the attraction curve and the repulsion curve will remain constant and the point of intersection will be determined by the triplet-singlet excitation energy of the olefin. The potential energy difference between the singlet A + R plateau region and the point of intersection refers to the activation energy of the addition process.

From Fig. 31 it can be seen that factors which influence the repulsive curve should also influence the reactivity. Electron withdrawing groups on the olefin should therefore reduce the charge density of the π -cloud and result in a flattening of the repulsive curve with a lowering of the activation energy. This prediction is confirmed experimentally. Tetrafluoroethylene was found to be 10 times more reactive than ethylene towards methyl radical addition (99). Chlorinated benzenes were also found to have larger methyl affinities than benzene (95).

Unlike the radical reagents, species such as $O(^3P)$, $Se(^3P)$, Br , and CF_3 show a drastic increase in reactivity with increased alkyl substitution on the double bond thus exhibiting electrophilic behavior (Table XIX). Unlike the radical reagents the reactivities of electrophilic reagents do not correlate with localisation energies i. e., with parameters related directly to the carbon centers. Rather, the reactivities correlate more closely to parameters dealing with the double bond as a whole such as ionisation potentials and excitation energies. The rate controlling process in these reactions therefore seems to involve polarisation of the olefin resulting in perhaps a charge-transfer complex being formed in the early stages of the reaction. Cvetanovic (100) proposed a charge-transfer π -complex as the transition state for addition of $O(^3P)$ atoms to olefins. An orientation of the $O(^3P)$ atom was indicated although this was suggested to occur after the initial formation of the rate controlling π -complex.

Stefani et al (101) observed a linear relationship between activation energy and ionisation potential for addition of CF_3 to

TABLE XIX
RELATIVE REACTIVITY OF ELECTROPHILIC REAGENTS
WITH A SERIES OF OLEFINS

Olefin	O(³ P) ^a	Se(³ P) ^b	Br ^c	CF ₃ ^d	Ionisation potential ^e	Excitation ^f energy
ethylene	1.0	1.0	1.0	1.0	10.62 ev	2.1498 - β units
ethylene-F ₄	-	-	-	0.15	-	-
propylene	5.8	2.6	18	2.8	9.84	2.0182
1-butene	5.8	7.1	23	3.5	9.76	2.0113
iso-butene	15.0	44.7	384	7.6	9.26	1.9164
<u>cis</u> -2-butene	23.8	23.9	95	0.60	9.34	1.9022
<u>trans</u> -2-butene	28.3	56	99	0.60	9.27	1.9022

a. Ref (100)

b. Ref (55)

c. Ref (104)

d. Ref (101)

e. Ref (78)

f. Ref (103)

olefins. They suggested that the electrophilic nature of CF_3 makes the polar structure olefin^+ , CF_3^- , important in describing the transition state of the addition process.

A potential energy diagram describing the reaction must contain a repulsive curve as postulated for the radical addition reactions and an attractive curve. The attractive curve in this case, however, must be electrostatic in nature to comply with the electrophilic nature of the reactive species.

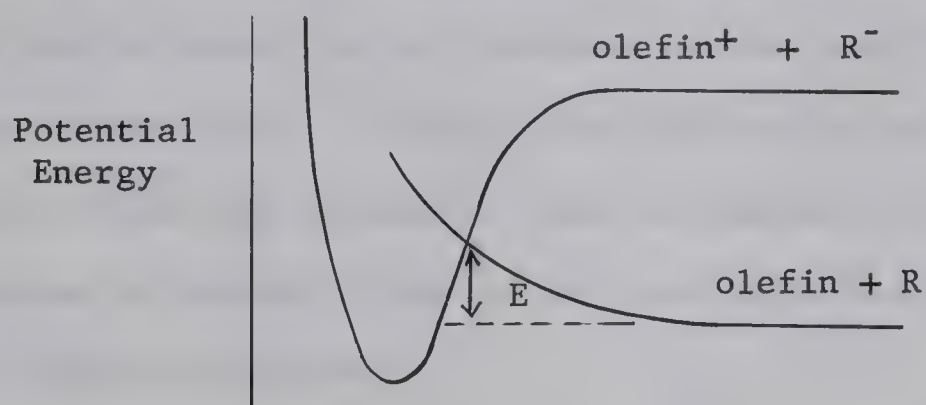


Fig. 32. Reaction Coordinate.

An increase in the electron density of the π -system will increase the slope of the repulsive curve, but this effect is counteracted by a decrease in the ionisation potential of the olefin thus reducing the activation energy of addition.

Although Szwarc, in an earlier paper (101), considered a π -complex as a transition state for the addition of CF_3 radicals, recently he has abandoned this idea in favor of the σ -complex suggested for radical reagents (102). Temperature studies indicate that a methyl or Cl substituent located on an olefinic hydrocarbon reduces the A factor of addition by ca. 5. This result is accounted for in terms of a restricted rotation around an incipient $\text{C}\cdots\text{CF}_3$ bond. The activation energy of CF_3 addition was found to be linear

with the ionisation potential but $\log k$ was not linearly related. While the ionisation potential and activation energy were determined only by the number of substituents and not their distribution, the entropy of activation did depend on the location of the methyl group. For this reason Szwarc concluded that the transition state of addition must be associated with a carbon atom rather than a C=C bond. He also suggested, on the basis of a linear correlation of activation energies for CF_3 and $\text{O}(^3\text{P})$ addition that $\text{O}(^3\text{P})$ addition also proceeds via a σ -complex rather than the π -complex proposed by Cvetanovic. Oxygen atom addition is isoentropic and Szwarc claims that arguments based on changes in activation energy alone may erroneously lead to the conclusion that a π -type transition state is involved.

i. Addition of $\text{S}(^3\text{P})$ atoms.

The increased reactivity of $\text{S}(^3\text{P})$ atoms with increasing alkyl substitution on the double bond clearly indicates the electrophilic nature of this atom. A good linear correlation of $\log k$ with ionisation potential of the olefin is obtained for α, α substituted olefins, although this correlation does not exist for α, β substituted olefins. Since activation energy and preexponential factor data are unavailable for this system these relative values can only be estimated by comparison of the relative rate data with that for other electrophilic species. Oxygen and CF_3 addition indicate that $\log k$ is linearly related to ionisation potential only for isoentropic additions (i.e., E_{act} also correlates with ionisation potential), while for non-isoentropic additions only E_{act} correlates with the ionisation

potential. By analogy with these systems it may be suggested that in the case of $S(^3P)$, addition is isoentropic to α, α but not α, β substituted olefins. From ionisation potential data it can also be suggested that the activation energies for addition of $S(^3P)$ to isobutene, and cis and trans-2-butenes are nearly identical while the entropy of activation for the 2-butenes is considerably lower as indicated by the lower $\log k$ values. Therefore, even without direct temperature data one can at least tentatively suggest that the lower addition rates to the 2-butenes probably arises from some form of steric hindrance to the reactive site of the molecule.

The primary interest of this discussion is the rate controlling step for the addition reaction and the reactive site of the olefin.

The rate of a reaction is dependent on two factors; the activation energy and the preexponential factor A . The factors which affect these two quantities will be discussed. Since the activation energy is linearly related to the ionisation potential it is therefore dependent on the type of substitution on the double bond. Addition of alkyl groups to the double bond increases the electron density of the π system with a resultant lowering of the ionisation potential and thus a decrease in the activation energy.

The chlorine atom is electron withdrawing, but the lower ionisation potential of vinyl chloride determines the activation energy with the result that vinyl chloride is more reactive than ethylene. Such a comparison must assume constant entropy of activation for the olefins compared.

The activation energy for the addition of $S(^3P)$ can be illustrated by the following diagram:

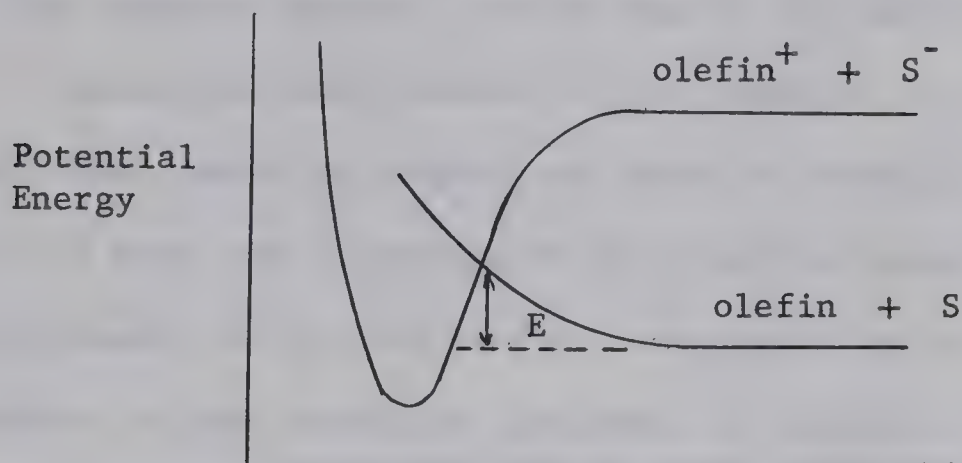


Fig. 33. Reaction Coordinate

The ease of formation of a charge transfer complex is directly related to the activation energy of addition and the transition state must involve participation of the ionic structure olefin^+ , $S(^3P)^-$.

The participation of a charge transfer complex in the transition state, however, does not necessarily mean that a π -complex describes the transition state. It only describes the nature of the attraction but does not indicate the reactive site of the molecule.

Addition of one methyl group to ethylene increased the reactivity by a factor of ca. 7. Addition of a second methyl group to the same carbon atom, giving isobutene, again resulted in a further increase in reactivity by a factor of ca. 7. However, addition of the second methyl group to the adjacent carbon, giving 2-butene, resulted in only a ca. 2.5 fold increase in reactivity. It was earlier suggested that the activation energy depended only on the amount of substitution and not its position. The lower

reactivity of both cis and trans-2-butenes therefore may be due to a decrease in the entropy of activation, resulting from the blocking of the reactive terminal carbon atom by the methyl group.

Since the final product of the addition is a triplet biradical the transition complex may involve formation of an incipient C---S bond, the formation of which may be hindered if a bulky group is present on the carbon atom. The main factor favoring a σ -complex is that the steric hindrance is dependent on the position of the substituent rather than on the number of substituents. If a π -complex is involved steric hindrance should be dependent on the amount of substitution on the double bond and not on its position since reactivity in this case concerns the double bond as a whole. This effect was not observed.

ii. Addition of $S(^1D)$ Atoms.

In view of the stereospecific addition of $S(^3P)$ atoms to olefins, it is no longer necessary to postulate that stereospecific addition of a singlet species to a double bond requires simultaneous formation of two bonds via a triangular transition state.

Although the data are only semi-quantitative, addition of $S(^1D)$ atoms to the double bond shows little or no electrophilic character but resembles radical reagents in reactivity. Like radical reagents then its reactivity might be expected to be greatest at points in the molecule displaying high electron density. Terminal carbon atoms are known to possess higher electron densities than non-terminal carbon atoms. Addition of $S(^1D)$ to an unsymmetrical double bond should then be expected to take place at the least

substituted carbon atom producing a singlet biradical. Ring closure would result in the observed episulfide product.

It was earlier suggested that such an orientation effect might be responsible for the formation of terminal vinylic mercaptans, since no non-terminal vinylic mercaptans were formed with unsymmetrical olefins.

CHAPTER VI

REACTIONS OF SULFUR ATOMS WITH ACETYLENE AND SUBSTITUTED ACETYLENES

1. Reaction of sulfur atoms with acetylene.
 - A. Static system.
 - B. Flash photolysis-kinetic mass spectrometry.
 - C. Flash photolysis - absorption spectroscopy.
 - D. Flow system.
2. Reaction of sulfur atoms with methyl acetylene.
 - A. Static system.
 - B. Flash photolysis-kinetic mass spectrometry.
3. Reaction of sulfur atoms with dimethyl acetylene.
 - A. Static system.
 - B. Flash photolysis-kinetic mass spectrometry.
 - C. Flash photolysis - absorption spectroscopy.
4. Reaction of sulfur atoms with perfluorobutyne-2.
 - A. Static system.
 - B. Flash photolysis-kinetic mass spectrometry.
5. Reaction of sulfur atoms with a mixture of acetylene and perfluorobutyne-2.
 - A. Static system.
6. Discussion.

RESULTS

ACETYLENE

A. Static System

When carbonyl sulfide was photolysed with acetylene, in low conversion runs, three condensible volatile products and a solid product were formed. The three volatile products had relative retention times of 1.00 (I) : 2:35 (II) : 2.75 (III) on an 8 ft. T.C.P. column. From their mass spectra they were identified as carbon disulfide, benzene and thiophene respectively. This was further confirmed by checking the retention times of pure carbon disulfide, benzene and thiophene with those of the products. All three products showed identical retention times with the authentic samples.

The reaction was studied as a function of acetylene pressure in the range 0 to 1000 torr. The CO yield is shown as a function of substrate pressure in Table XX and Figure 34. The CO yield decreases with increasing substrate pressure and at a pressure of 1000 torr it has reached the limiting value of $R^0(\text{CO})/2$. The yield of volatile condensible products was found to be very small (ca. 5%), the major product of the reaction being a yellow insoluble solid. This solid was similar to one found in the photolysis of acetylene at short wavelengths (105). In both cases the solid was found to be a hard yellow varnish-like substance (probably trans-polyacetylene).

TABLE XX

VARIATION IN PRODUCT YIELDS WITH ACETYLENE
PRESSURE IN THE COS-ACETYLENE SYSTEM^a

P(C ₂ H ₂)	Yields, μ moles/30 min.				
	CO ^b	CO ^o -CO ^b	CS ₂ ^c	Benzene ^c	Thiophene ^c
0	9.63	0	-	-	-
25.1	6.81	2.82	137	0	0
53.6	6.52	3.11	124	0	0
103.4	5.80	3.83	81	0	0
201.4	5.52	4.11	45	8	19
319.4	5.80	3.83	40	29	10
640	5.18	4.45	21	37	6
998	4.70	4.93	14	41	0

a. P(COS) = 100 torr; Exposure time = 15 min.; Medium pressure mercury arc.

b. Measured in μ moles.

c. Measured in arbitrary units.

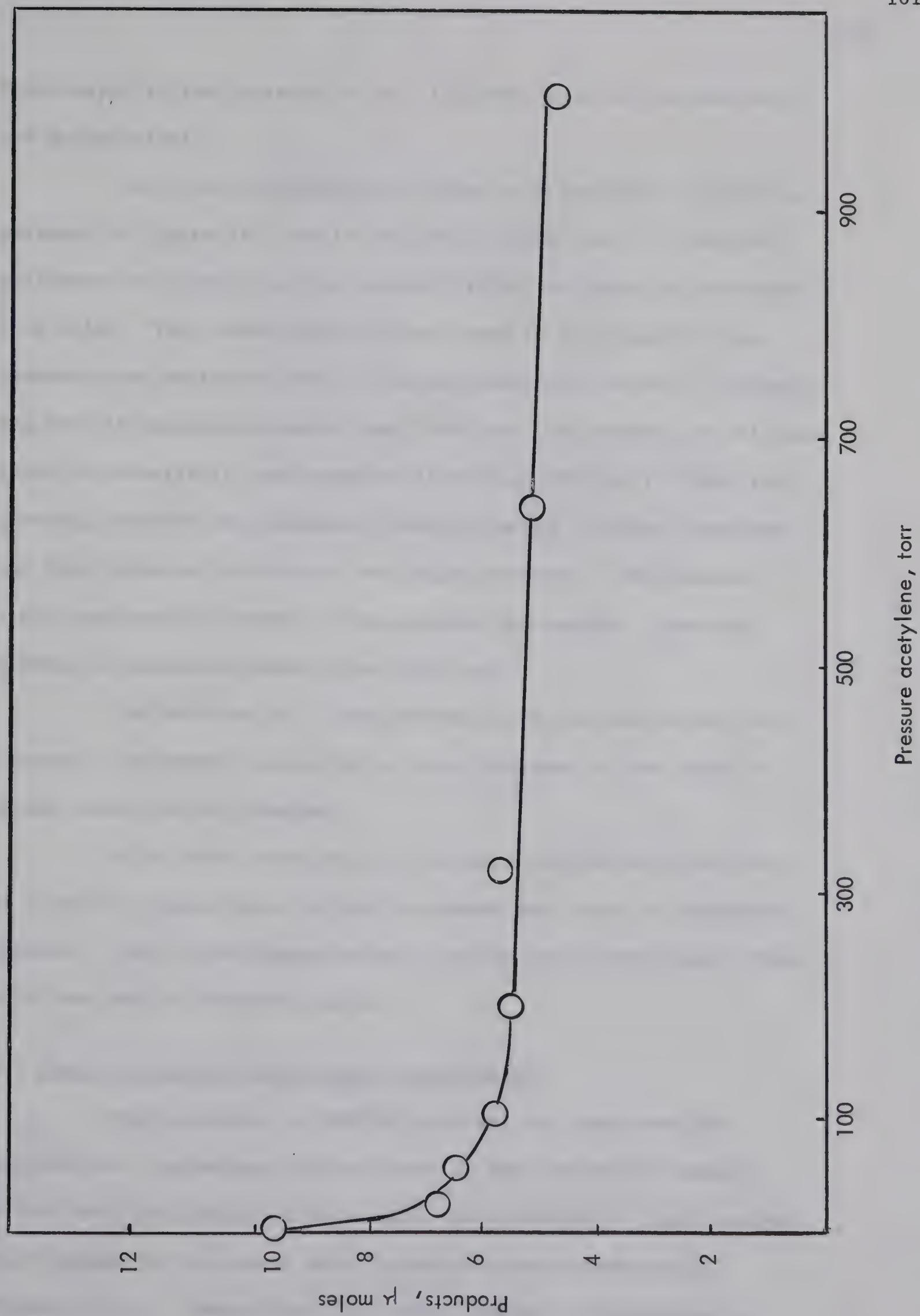


Fig. 34 CO formation as a function of acetylene pressure.

When heated in the presence of air it turned to a dark colored solid and burned slowly.

The volatile products are shown as a function of substrate pressure in Figure 35. Due to the small yields the G. C. was not calibrated in μ moles but the product yields are given in arbitrary area units. The carbon disulfide was found to be largest at low pressures and decreased with increasing substrate pressure, approaching zero at pressures greater than 1000 torr. No benzene or thiophene could be detected at low pressures (less than 100 torr). With increasing pressure the thiophene yield increased, reached a maximum and then decreased to zero at very high pressures. The benzene yield continued to increase with pressure and reached a constant maximum at pressures greater than 1000 torr.

The addition of a large excess of CO_2 did not affect the benzene or thiophene yields, but a large decrease in the yield of carbon disulfide was observed.

Solid phase photolysis of carbonyl sulfide and acetylene, at liquid N_2 temperature, failed to produce any volatile condensible products. Only carbon monoxide and a yellow solid were found. This solid was partly elemental sulfur.

B. Flash Photolysis-Kinetic Mass Spectrometry

When a mixture of COS(226 microns) and acetylene(800 microns) was flashed near the entrance to the ionization chamber of the mass spectrometer four products were observed. Time resolved oscillograms of the parent mass intensities are reproduced in Figures 36 - 41. Mass 58 was the major product corresponding to

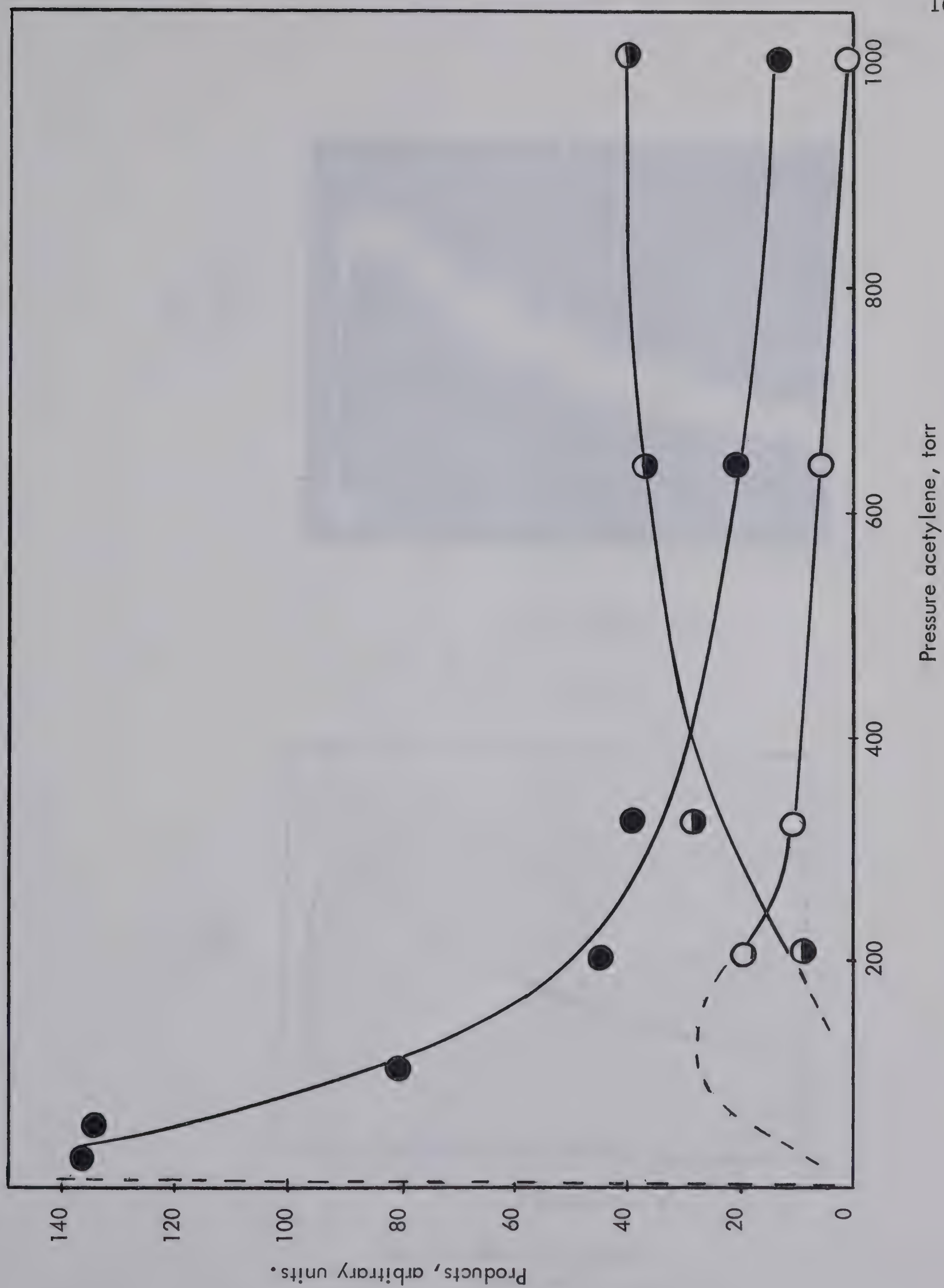
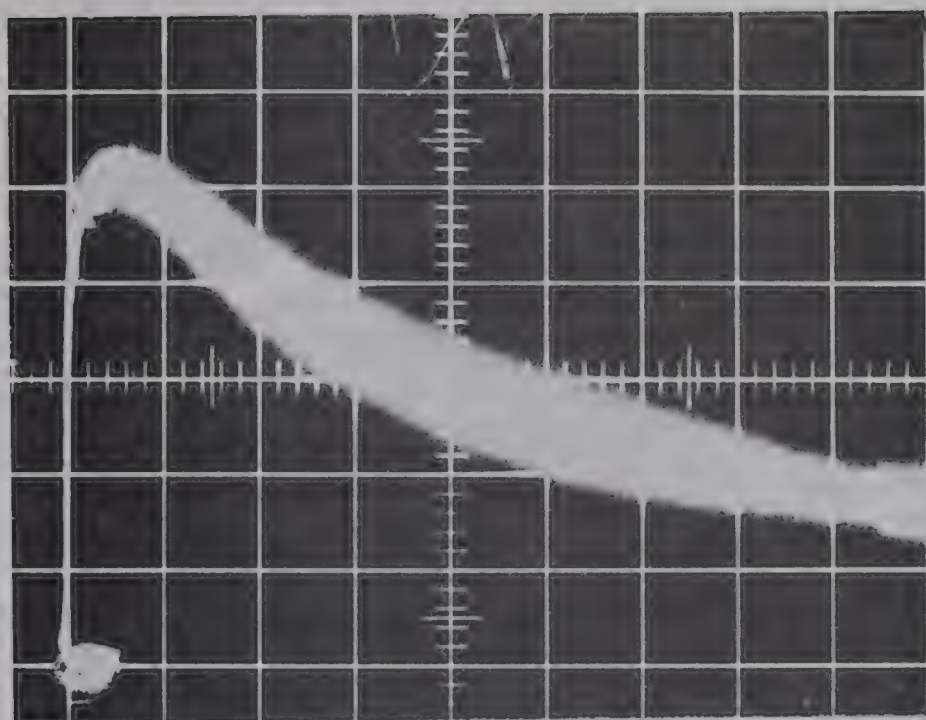


Fig. 35 Product formation as a function of acetylene pressure.

● = carbon disulfide; ◐ = benzene; ○ = thiophene.

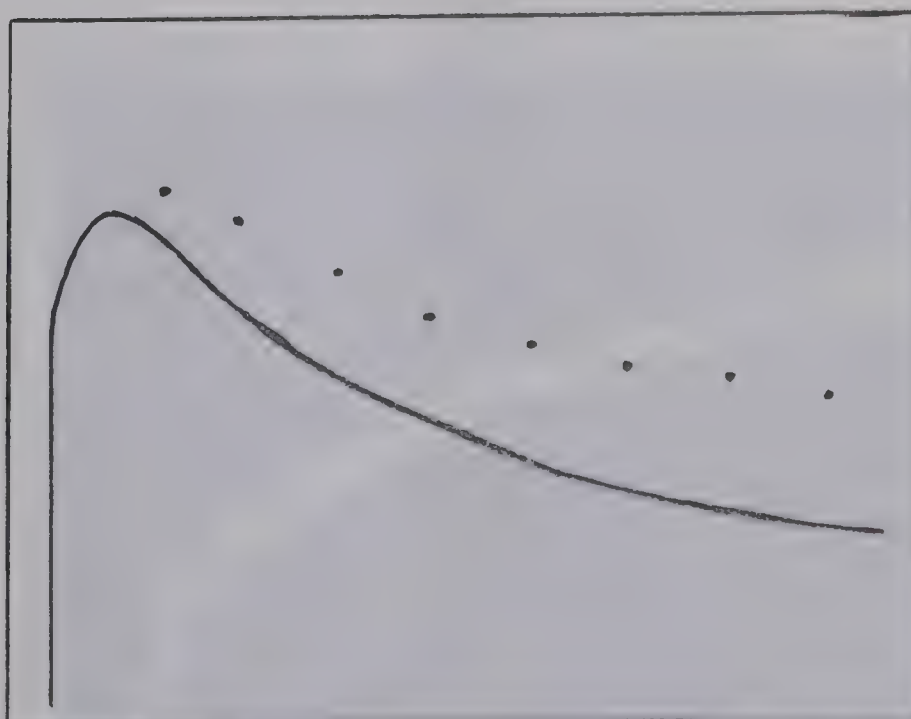
0.5 volts
per div.



0.2 Seconds per div.

Fig. 36 Mass 58, C_2H_2S

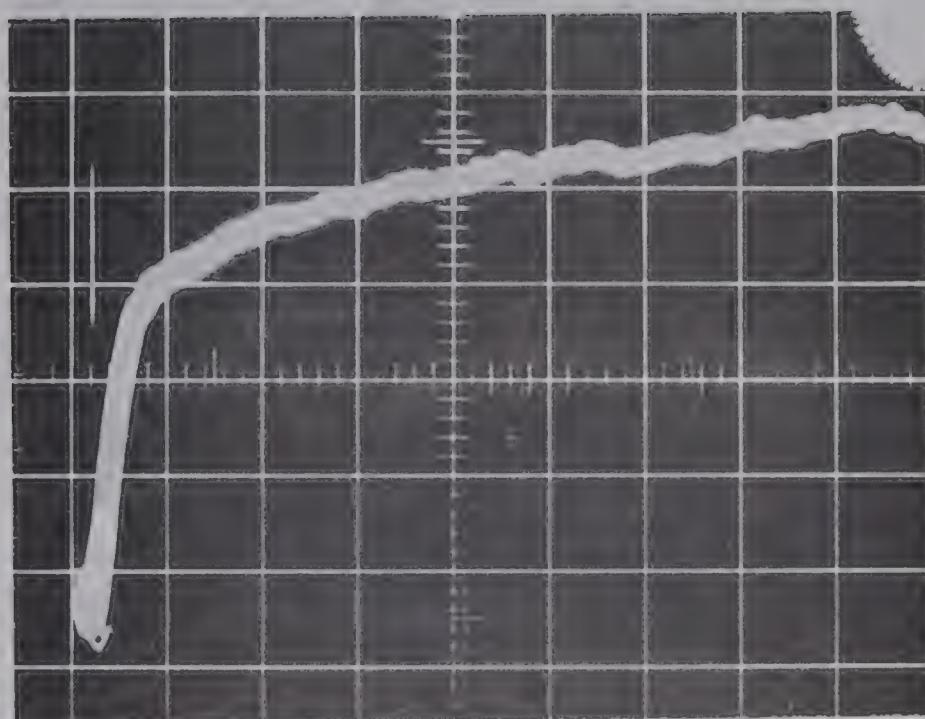
0.5 volts
per div.



0.2 Seconds per div.

Fig. 37 Mass 58, C_2H_2S
Corrected for bleed-out.

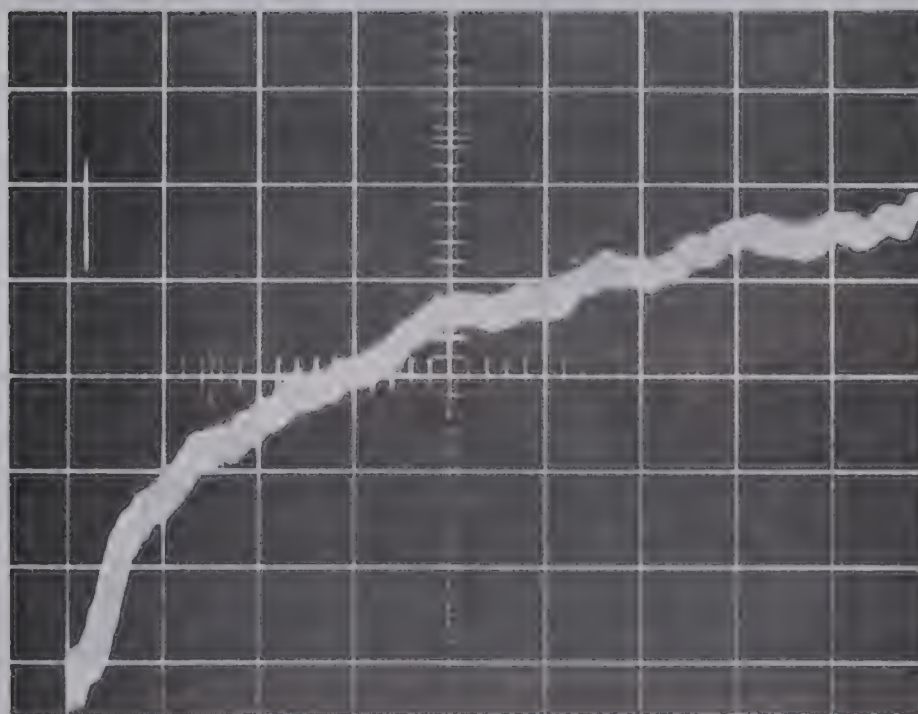
0.5 Volts
per div.



10.0 Milliseconds per div.

Fig. 38 Mass 58, C_2H_2S

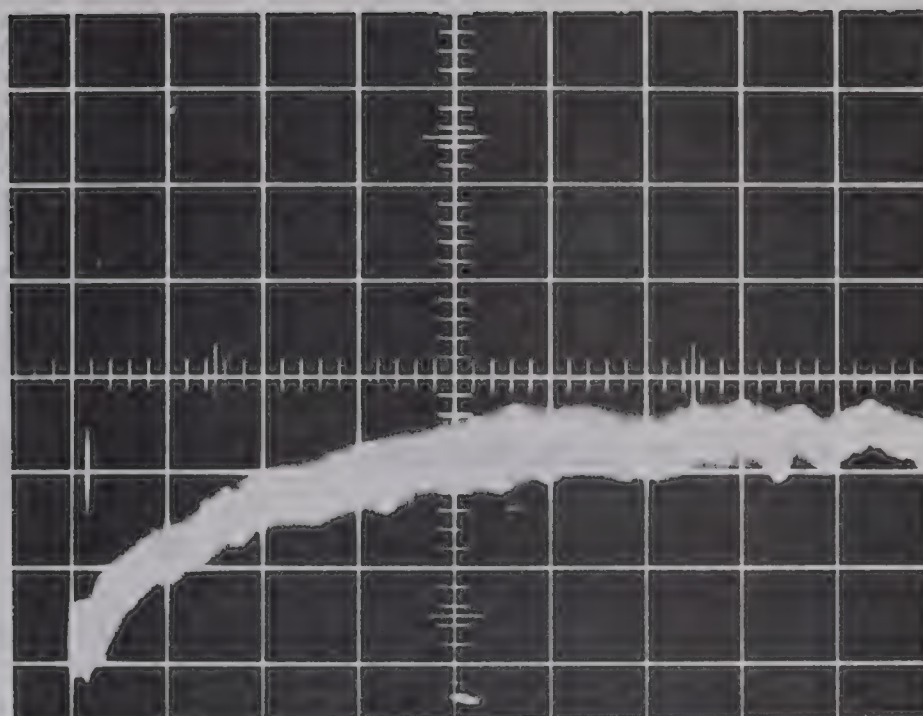
0.2 Volts
per div.



10.0 Milliseconds per div.

Fig. 39 Mass 76, Carbon Disulfide

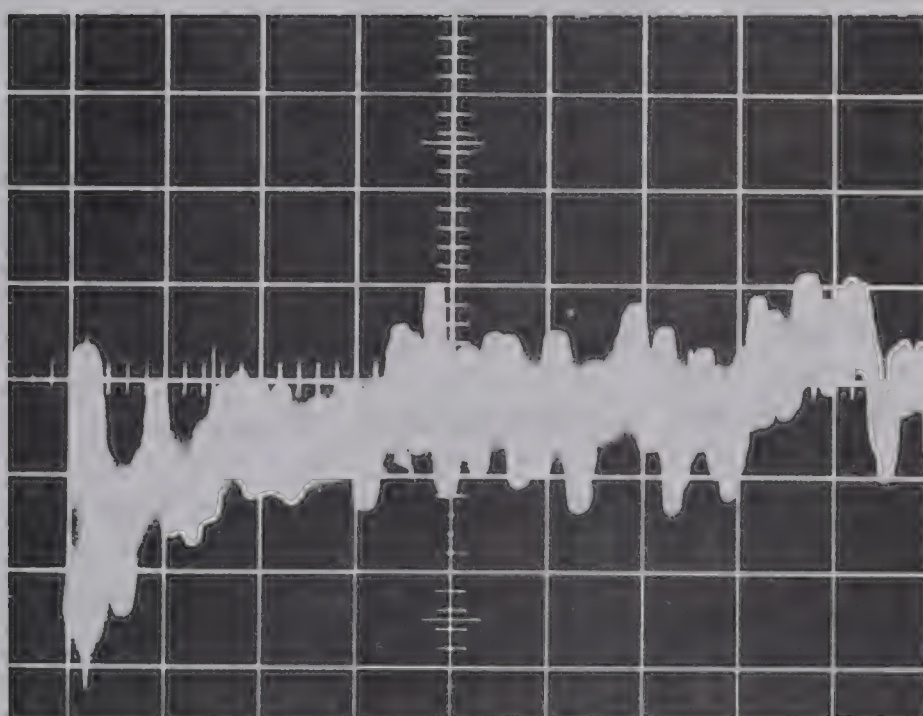
50.0
Millivolts
per div.



20.0 Milliseconds per div.

Fig. 40 Mass 78, Benzene

50.0
Millivolts
per div.



20.0 Milliseconds per div.

Fig. 41 Mass 84, Thiophene

the adduct C_2H_2S ; a product which was not observed in the static system. The C_2H_2S signal increased rapidly, reaching a maximum value of 2.7 volts after ca. 100 milliseconds. The signal, after correction for bleed-out, showed appreciable decay after 2 seconds as shown in Figure 37.

A second product of mass 76, corresponding to carbon disulfide, was also observed in large concentration; after ca. 100 milliseconds its signal reached a maximum value of 1.0 volts (Figure 39). A comparison of Figures 38 and 39 indicates that while the C_2H_2S signal reached its maximum value almost immediately (after ca. 25 milliseconds) the CS_2 signal grew slowly but continuously for the entire 100 millisecond period.

Benzene was found in a much smaller concentration, its maximum signal being 0.1 volts after 100 milliseconds. Figure 40 shows that, like CS_2 , the benzene signal grew slowly up to its maximum value, attained at ca. 100 milliseconds.

Thiophene, mass 84, was found in only a small concentration; the signal in Figure 41 was appreciably larger than the background signal indicating formation of this product. The formation of thiophene did not show the slow steady increase exhibited by both CS_2 and benzene but appeared to be formed at a rate comparable to that of the initial C_2H_2S adduct. Due to the large background noise of this weak signal, however, this fact cannot be established with complete certainty, but is only indicated by the large initial signal observed after only a few milliseconds.

C. Flash Photolysis - Absorption Spectroscopy

A mixture of 100 torr COS and 100 torr C₂H₂ in a 50 cm. cell was flashed and the absorption spectrum of the flashed mixture was recorded at times varying from zero to 18 milliseconds. The spectra are shown in Figure 42. The only change in the spectra, from that of pure COS, was the absorption at 2576 Å corresponding to the CS radical (106). From optical density measurements, and using Gaydon's (106) value of 3.8×10^{-10} cm²/molecule for the extinction coefficient for CS, the concentration of CS was found to be less than 10^{-5} μ moles per flash. Approximately 2 μ moles of COS was decomposed per flash indicating that CS is formed in negligible amounts.

Analysis of the condensible products after 10 flashes showed that 20 μ moles of CO and 6 μ moles of CS₂ were the only products. Due to the small quantities of CS detected it is evident that it cannot be a precursor to the CS₂ formation. Probably CS arises from the secondary photolysis of the CS₂ in the reaction system.

A second series of experiments, using the same substrate concentrations, was performed in which the reaction mixture was frozen in liquid nitrogen a few seconds after the flash. It was hoped that the C₂H₂S intermediate, having a lifetime of several seconds (as indicated by flash photolysis-kinetic mass spectrometry) might be trapped and stabilized by this technique. Mass spectral analysis of the condensible products showed, however, no C₂H₂S product but only CS₂ as found in the previous experiment.

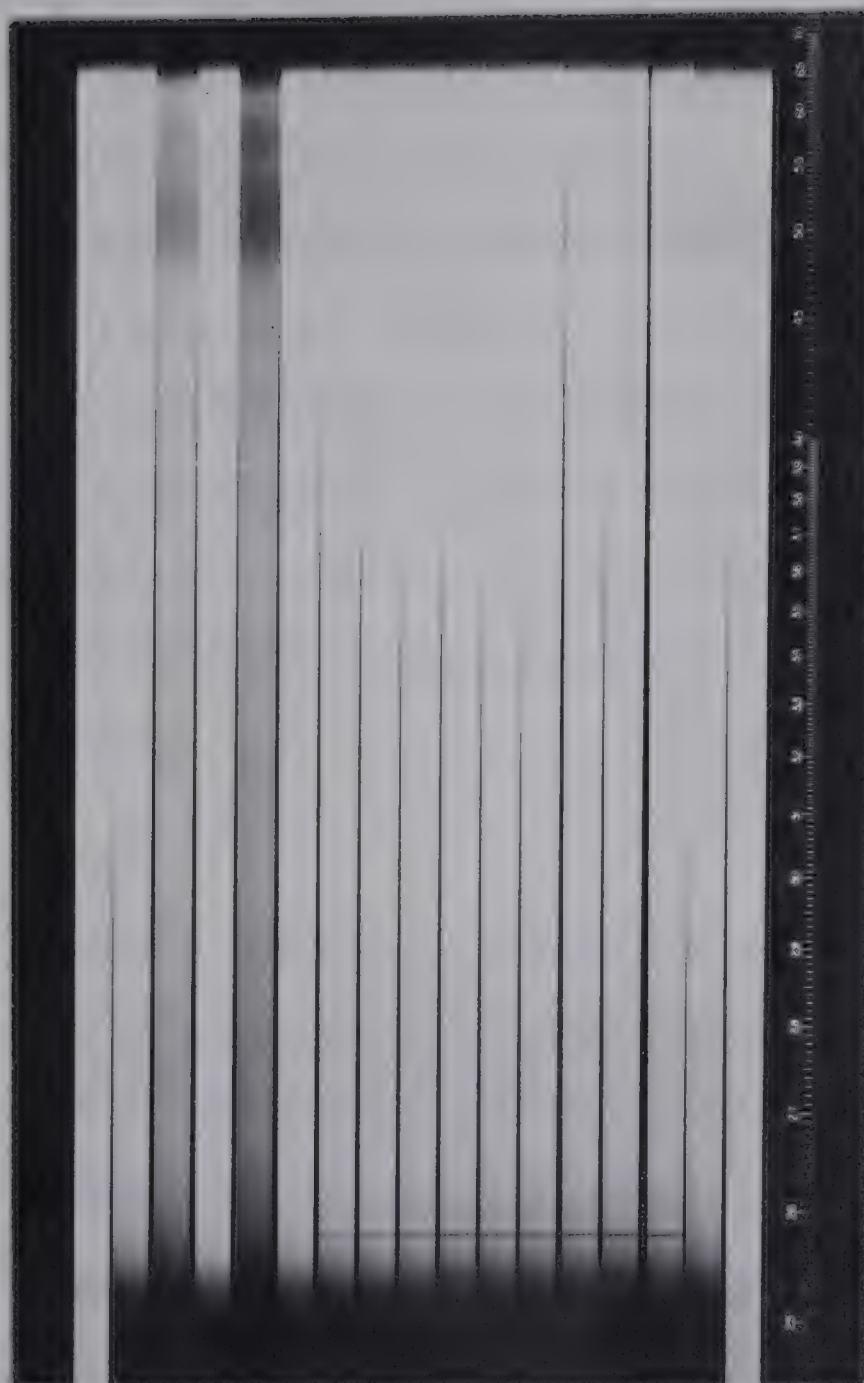


Fig. 42 Absorption spectrum of Flashed Mixture of COS and Acetylene.
Absorption at 2576 Å due to the CS radical.

The time required to freeze out the products together with the time required to obtain the mass spectrum of the reaction products would probably be very large compared to the life-time of the C_2H_2S product. For this reason the above technique was probably inadequate for detection of the C_2H_2S species.

Flash photolysis of a mixture of 700 torr COS and 700 torr C_2H_2 again yielded CO and CS_2 as the only products of the reaction. The high pressure system was observed to decrease the amount of CS_2 relative to CO. A set of flashes yielded 40 μ moles of CO while only ca. 3 μ moles of CS_2 was formed. This is approximately a four-fold decrease in CS_2 formation as compared to the low pressure region.

D. Flow System

A mixture of COS and acetylene was photolysed in a flow system at a total pressure of ca. 1 torr and the reaction products were frozen in liquid nitrogen immediately after photolysis, in a U-trap at the exit end of the flow system. The COS and acetylene were then removed at $-131^\circ C$ leaving behind only the products (including unstable intermediates) of the reaction. Methyl acetylene was then added to the products at $-131^\circ C$ and the total mixture was allowed to warm to room temperature. The methyl acetylene was then removed and the condensible products were analysed. Product analysis showed that trimethyl benzene was formed in this reaction in a small yield. No other products were detected.

METHYL ACETYLENE

A. Static System

Photolysis of carbonyl sulfide in the presence of methyl acetylene, in low conversion runs, yielded as the major product a yellow non-volatile solid similar to that found in the acetylene reaction. Condensable volatile products corresponding to 5% or less of the sulfur atoms consumed were also obtained. Analysis by low energy mass spectrometry showed two parent peaks at masses 112 and 120. These would correspond to a dimethyl thiophene and a trimethyl benzene respectively and in light of the results obtained for acetylene these masses were tentatively assigned to these products. Assuming the same sensitivities of both compounds towards the mass spectrometer, the dimethyl thiophene was found to be the major product, the trimethyl benzene forming ca. 30% of the total. This assumption is probably valid to within a factor of two.

Gas chromatographic analysis of the condensibles showed at least two isomers of each compound present although due to the small amount of products formed their isomeric analysis was not attempted. G. C. analysis also showed the dimethyl thiophene present in the larger amount.

The non-condensable fraction contained only CO; no H₂ or other non-condensable product was formed in the reaction. Careful analysis also showed that no ethylene or acetylene was produced. These products were specifically sought in light of recent results obtained in the reaction of O(³P) with methyl acetylene where large

amounts of ethylene and acetylene were formed (107). Addition of $S(^1D)$ or $O(^3P)$ to methyl acetylene produces adducts of nearly equal excitation energies.

Unlike the acetylene system, no CS_2 was found as a product. Addition of a large excess of inert gas, CO_2 , failed to increase the condensible product yield.

A search for C_3H_4S products failed to indicate formation of stable sulfur adducts resulting either from addition to the triple bond or insertion into the C-H bonds.

CO formation was found to drop rapidly upon addition of methyl acetylene (Table XXI and Figure 43), reaching its limiting value of $R^O(CO)/2$ at a value of 2 for the ratio C_3H_4/COS .

B. Flash Photolysis-Kinetic Mass Spectrometry

Time resolved oscillograms of parent masses, produced when a mixture of COS (400 microns) and methyl acetylene (800 microns) was flashed, are shown in Figures 44 - 47. The major product, mass 72, was the sulfur adduct of methyl acetylene C_3H_4S . The signal, corrected for bleed-out, showed appreciable decay. The oscillogram indicated a half-life of ca. 5 seconds for the C_3H_4S product.

Dimethyl thiophene (Fig. 46) and trimethyl benzene (Fig. 47) were also detected, although in considerably reduced yields compared to the sulfur adduct.

TABLE XXI

CO FORMATION AS A FUNCTION OF SUBSTRATE PRESSURE
IN THE COS-METHYL ACETYLENE SYSTEM^a

P(COS) torr	P(C ₃ H ₄) torr	CO μ moles
100	0	15.5
100	68	8.6
100	128	8.3
100	290	7.5
100	667	7.7

a. Medium pressure mercury arc.

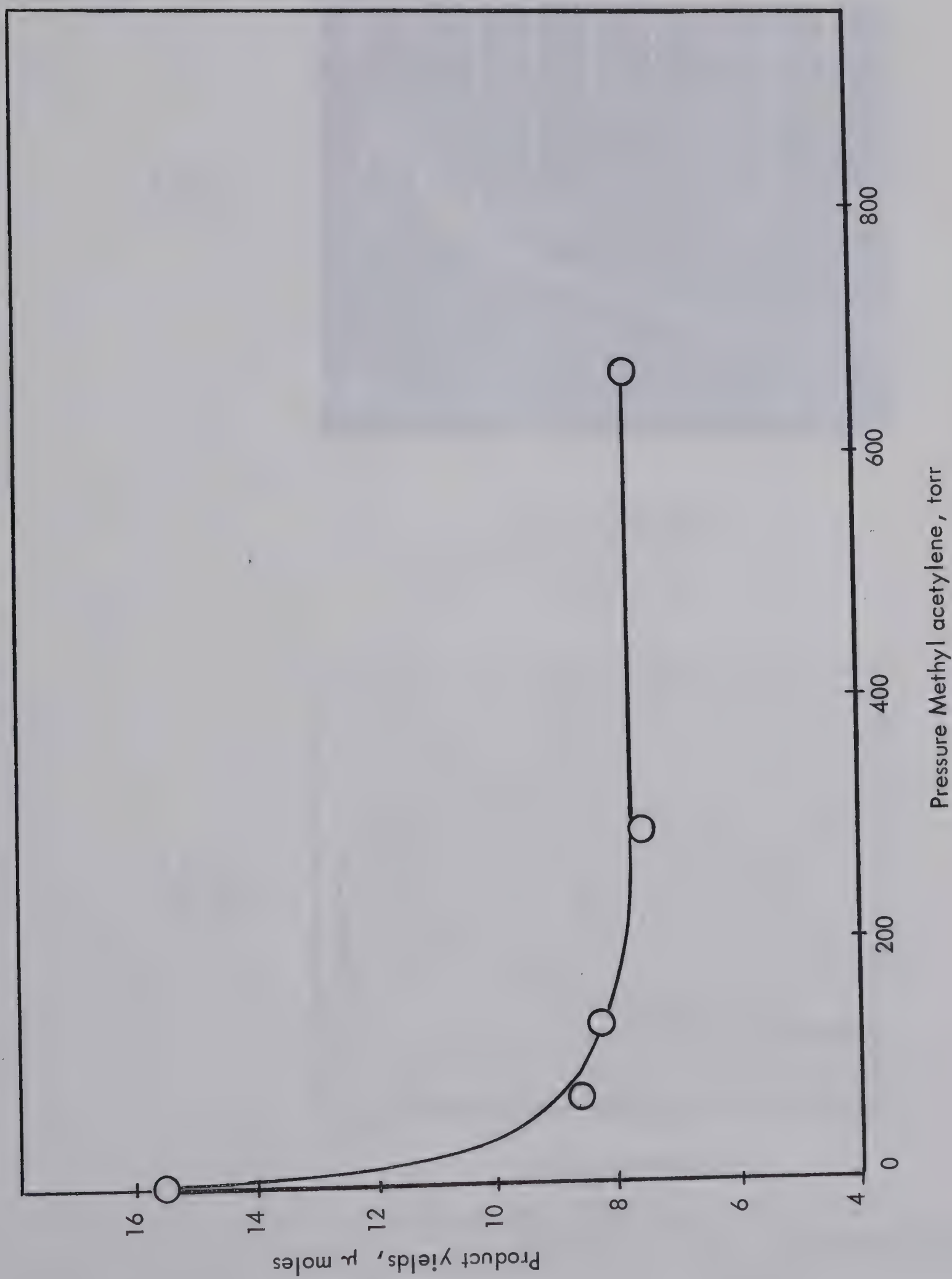
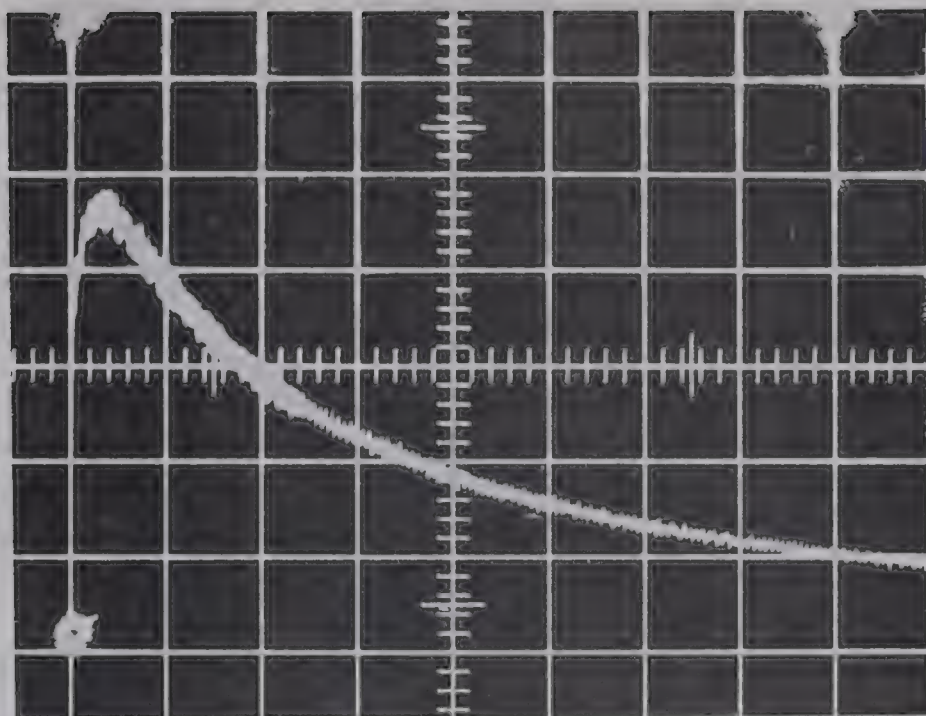


Fig. 43 CO formation as a function of methyl acetylene pressure.

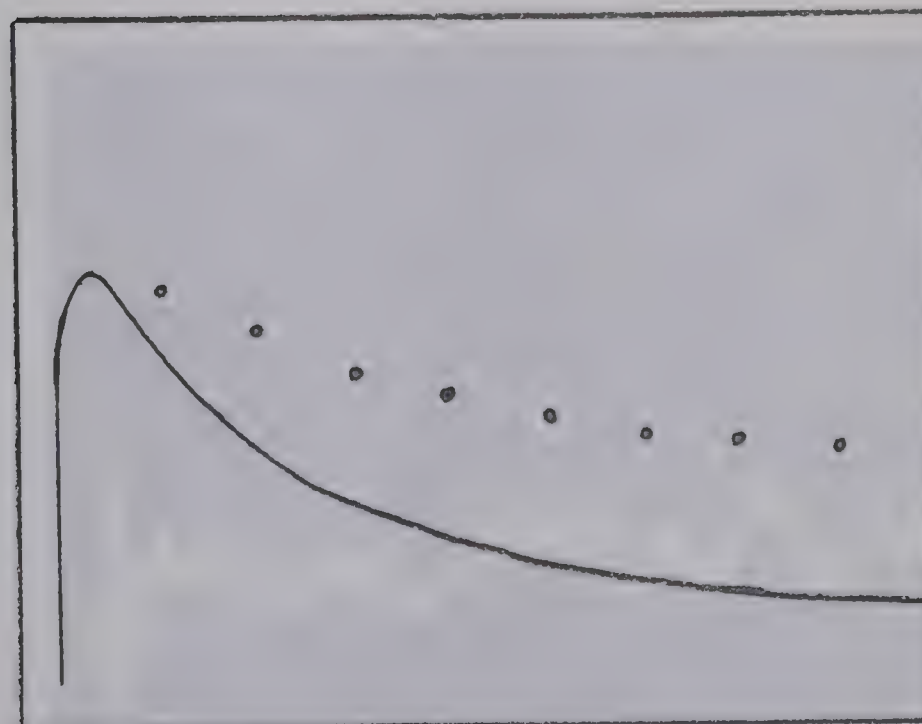
2.0 volts
per div.



0.5 Seconds per div.

Fig. 44 Mass 72, C_3H_4S

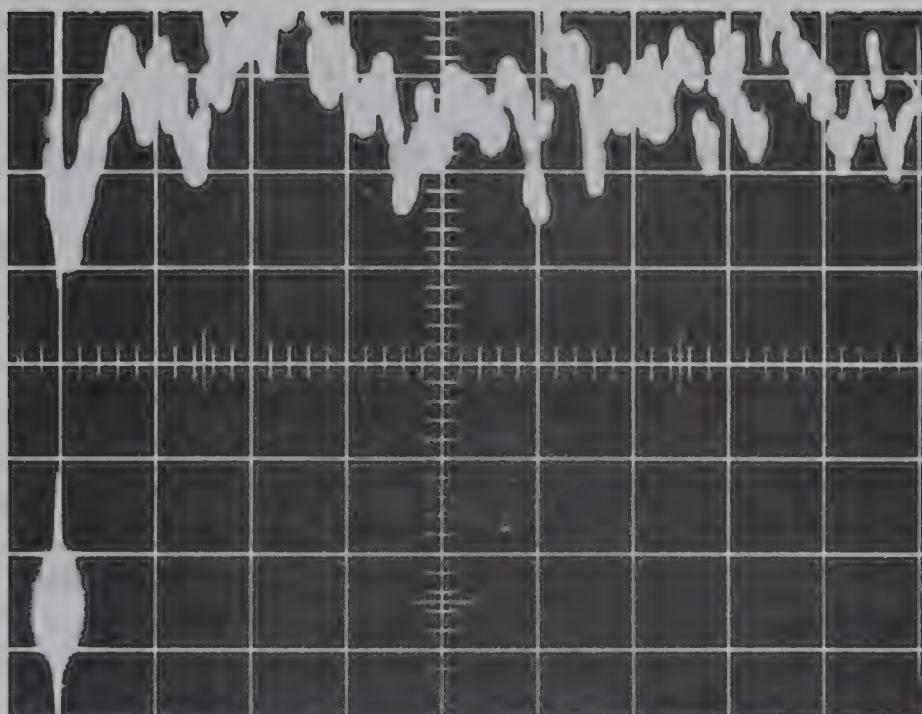
2.0 volts
per div.



0.5 Seconds per div.

Fig. 45 Mass 72, C_3H_4S
Dotted line is signal corrected for bleed-out.

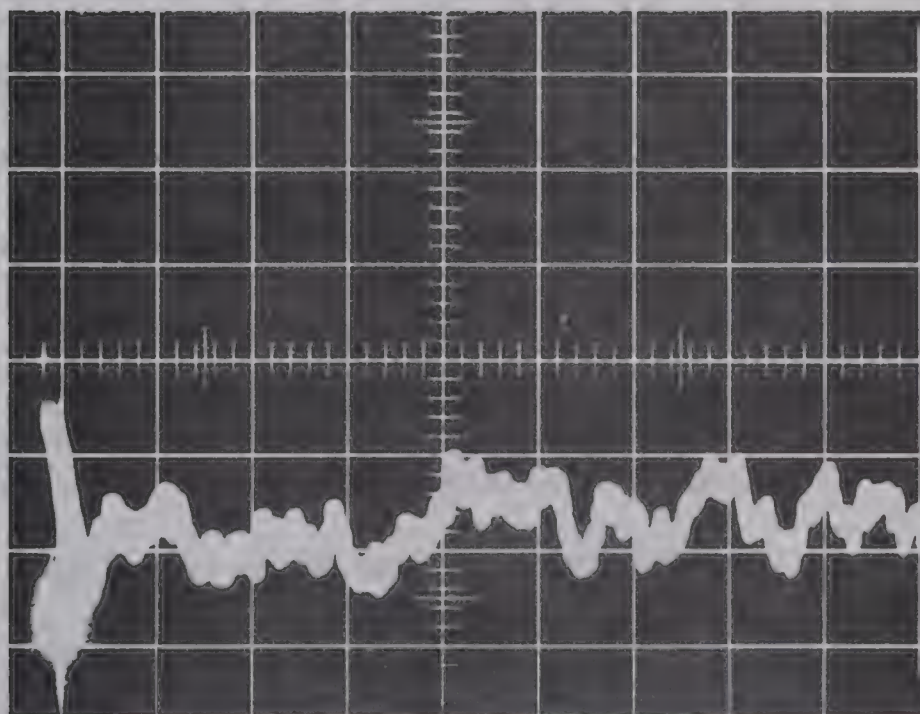
50.0
Millivolts
per div.



10.0 Milliseconds per div.

Fig. 46 Mass 112, dimethyl thiophene

50.0
Millivolts
per div.



10.0 Milliseconds per div.

Fig. 47 Mass 120, trimethyl benzene

DIMETHYL ACETYLENE

A. Static System

The reaction of sulfur atoms with dimethyl acetylene produced only one product in a yield of 5% or less, in terms of sulfur atoms consumed. This product was found by mass spectrometry to have a parent mass of 140 and was thus identified as the tetramethyl thiophene. Unlike the previous acetylene reactions no substituted benzene was found with dimethyl acetylene. The expected product, hexamethyl benzene, is a solid of melting point 166°C and if produced in the reaction in small yields might have gone undetected.

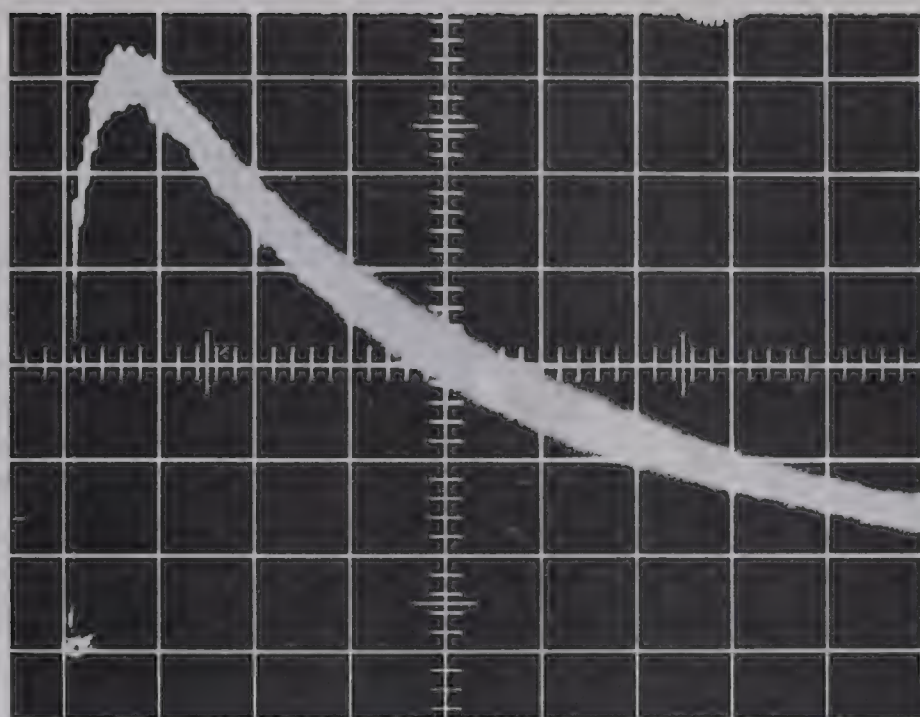
No addition or insertion product, $\text{C}_4\text{H}_6\text{S}$, was observed in this system. Again the major product was a non-volatile solid deposited on the walls of the cell.

B. Flash Photolysis-Kinetic Mass Spectrometry

A mixture of COS (400 microns) and dimethyl acetylene (800 microns) was flashed and the observations recorded on oscillograms 48 - 51. The adduct was shown to be formed in a large concentration (Figure 48). From the corrected oscillogram the half-life of this species was calculated to be ca. 7 seconds. Tetramethyl thiophene was detected in small concentrations.

Since $\text{S}(^1\text{D})$ atoms are known to insert into C-H bonds, this $\text{C}_4\text{H}_6\text{S}$ signal may be due to an insertion product as well as to addition to the triple bond. To investigate the reactivity of S atoms with the triple bond, photolysis of ethylene episulfide was used as the source of sulfur atoms. It has been shown that

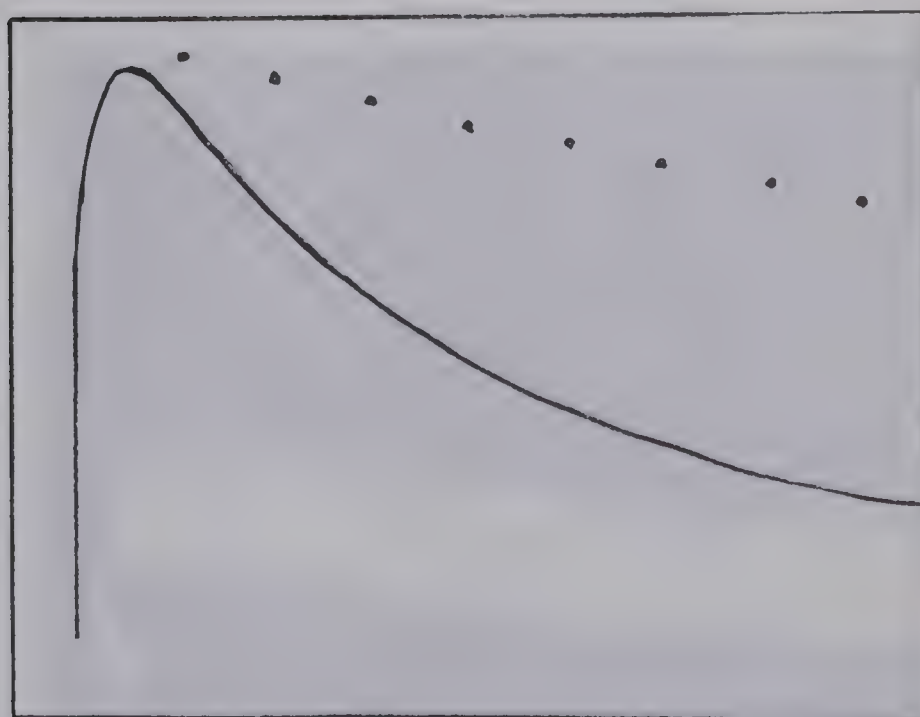
1.0 volts
per div.



0.5 Seconds per div.

Fig. 48 Mass 86, C_4H_6S

1.0 volts
per div.

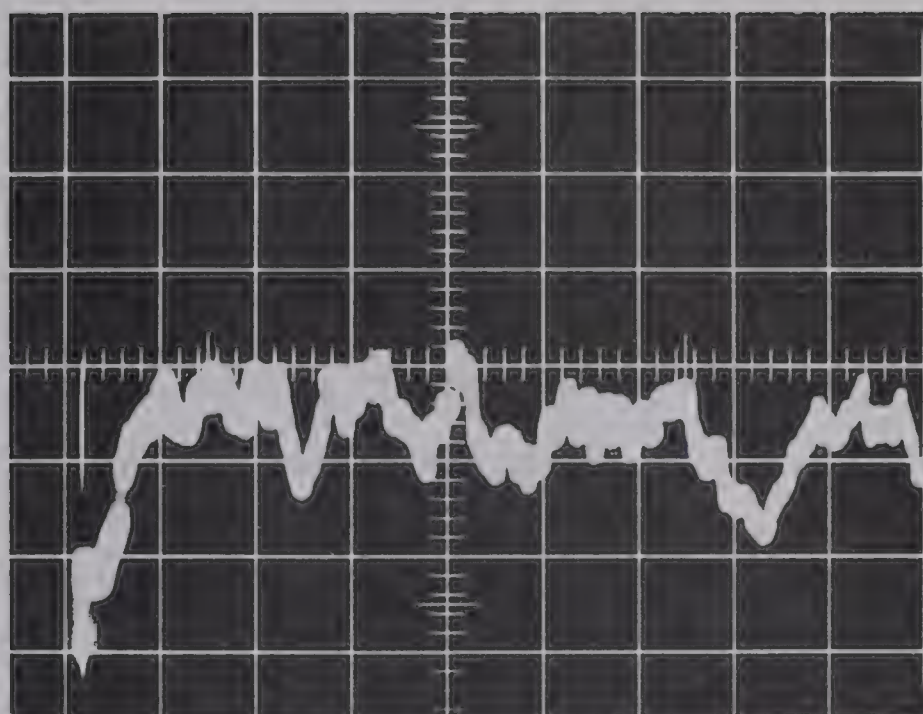


0.5 Seconds per div.

Fig. 49 Mass 86, C_4H_6S

Dotted line corrected for bleed-out.

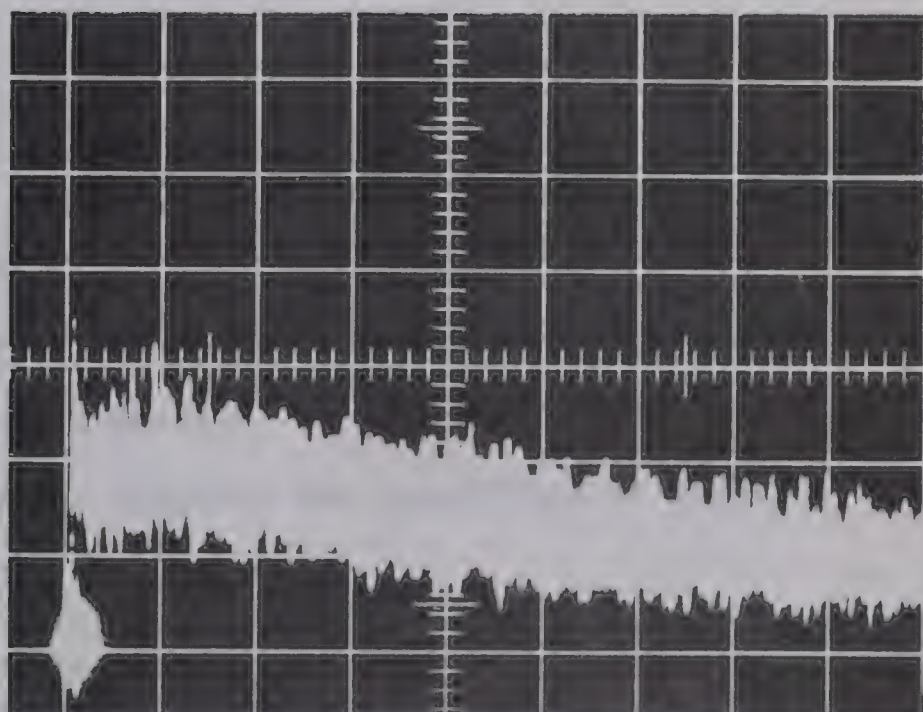
50.0
Millivolts
per div.



10.0 Milliseconds per div.

Fig. 50 Mass 140, tetramethyl thiophene

50.0
Millivolts
per div.



0.5 Seconds per div.

Fig. 51 Mass 140, tetramethyl thiophene

ethylene episulfide yields only ground state $S(^3P)$ atoms which are inert towards C-H bonds (108). The mixture consisted of C_2H_4S (400 microns) and dimethyl acetylene (800 microns). The results are shown in Figures 52 and 53. Again the large signal for mass 86 is observed indicating a C_4H_6S adduct resulting from addition of $S(^3P)$ to the triple bond of the acetylene. The half-life is found to be ca. 7 seconds in this case also.

C. Flash Photolysis

A mixture of 100 torr COS and 100 torr dimethyl acetylene was flashed and the absorption spectra recorded at various time delays as shown in Figure 54. No new spectra were observed. It is important to note also that no trace of CS absorption was observed in this reaction.

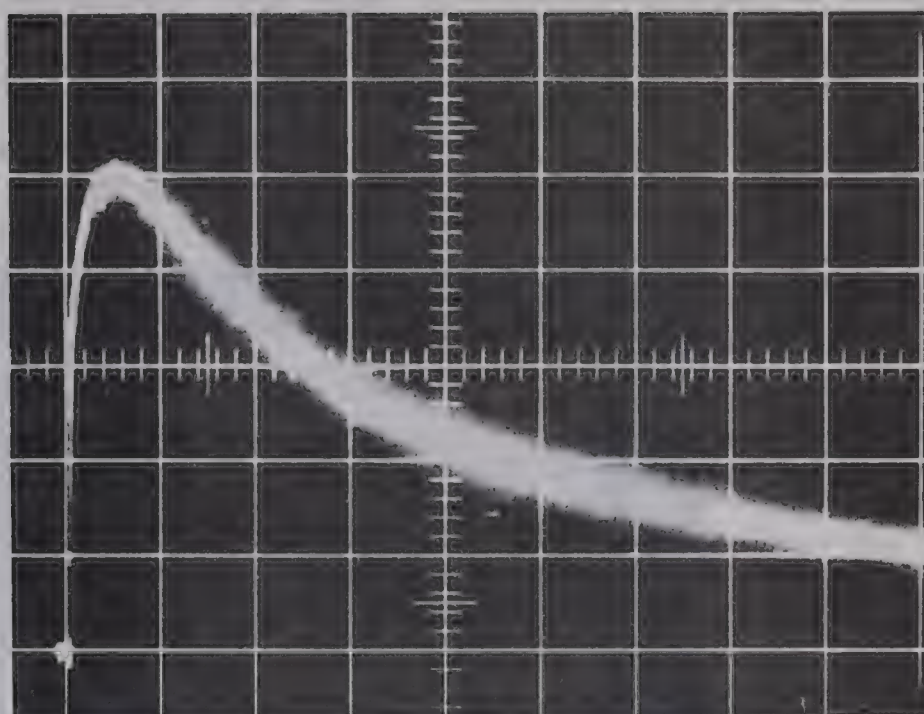
PERFLUOROBUTYNE-2

A. Static System

Photolysis of carbonyl sulfide with perfluorobutyne-2 produced only one volatile condensible sulfur-containing compound. Mass Spectrometric analysis of this compound showed a parent mass of 356 and the compound was identified as perfluoro-tetramethyl thiophene.

No C_4F_6S product was found in the static system. Perfluorohexamethyl benzene was not found in this reaction although, as its physical properties are not known, it may be a solid of low volatility and thus have escaped detection.

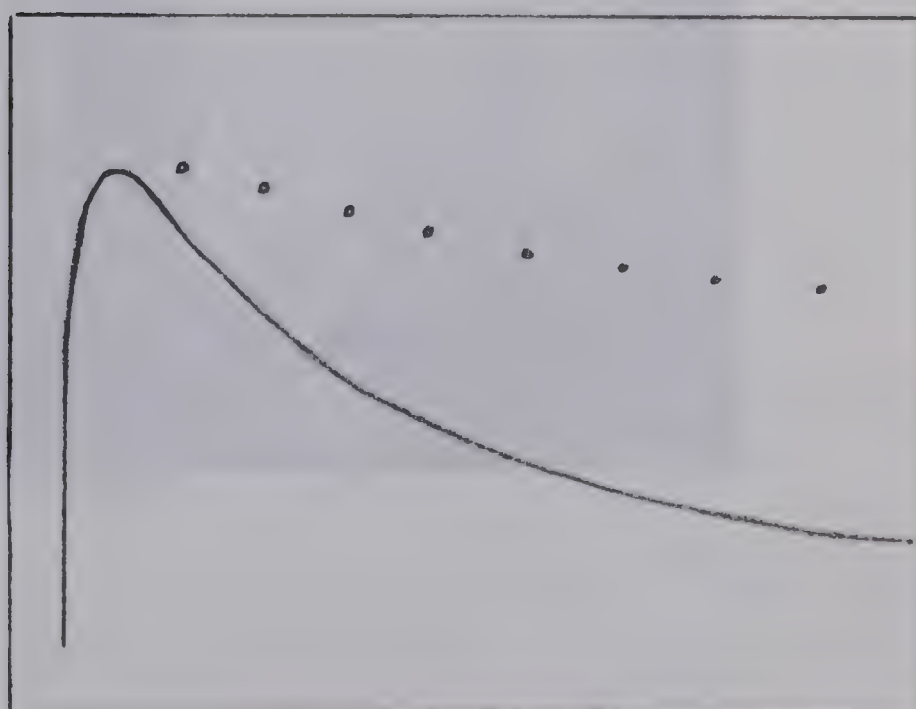
2.0 volts
per div.



0.5 Seconds per div.

Fig. 52 Mass 86, C_4H_6S

2.0 volts
per div.



0.5 Seconds per div.

Fig. 53 Mass 86, C_4H_6S
Dotted line corrected for bleed-out.



Fig. 54 Absorption Spectrum of Flashed Mixture of COS and Dimethyl Acetylene.

The reaction was studied as a function of substrate pressure and carbon dioxide pressure. Table XXII and Figure 55 show the variation of carbon monoxide with added substrate pressure. The CO decreases with increasing pressure and at high pressures approaches the limit of $R^O(\text{CO})/2$. At the same time the yield of perfluorotetramethyl thiophene increases continuously, (Fig. 56) its yield is ca 50% (in terms of S atoms consumed) at a pressure of 400 torr and is seen to be still rising. Extrapolation to infinite pressure would give a yield of at least 70%.

The addition of the inert gas CO_2 is found to have only a small effect. Table XXIII and Figure 57 show a small decrease in carbon monoxide and a similarly small decrease in the yield of perfluorotetramethyl thiophene.

B. Flash Photolysis-Kinetic Mass Spectrometry

Time resolved oscillograms, shown in Figures 58 - 60, show that a $\text{C}_4\text{F}_6\text{S}$ adduct is formed when a mixture of COS (400 microns) and perfluorobutyne-2 (800 microns) was flashed. Figure 58 shows a rapid increase in the mass 194 signal followed by a rapid decay after only a few milliseconds. This effect is more obvious in Figure 59; the signal drops rapidly to ca. two thirds of its maximum value and then decreases at a much reduced rate. Figure 60, corrected for bleed-out, shows an almost stable signal after the initial rapid drop. This is unlike the signals observed for acetylene, methyl acetylene and dimethyl acetylene where the initial fast drop did not occur but the signals rose to a maximum during the first 100 milliseconds.

TABLE XXII

VARIATION IN PRODUCT YIELDS WITH PERFLUOROBUTYNE-2
PRESSURE IN THE COS-PERFLUOROBUTYNE-2 SYSTEM^a

P(C ₄ F ₆) torr	Yield, μ moles			% Recovery ^c
	CO	CO ^O -CO	C ₈ F ₁₂ S ^b	
0	6.96	0	0	0
42.5	5.09	1.86	0.36	19
83.6	4.76	2.19	0.62	28
83.6	4.60	2.35	0.66	28
135.9	4.42	2.53	0.85	34
187.4	4.21	2.74	1.05	38
288.3	4.07	2.88	1.33	46
383	3.98	2.98	1.50	50

a. P(COS) = 100 torr; Exposure times = 30.0 min. Cadmium lamp.

b. Perfluorotetramethyl thiophene

c. In terms of R^OCO-RCO

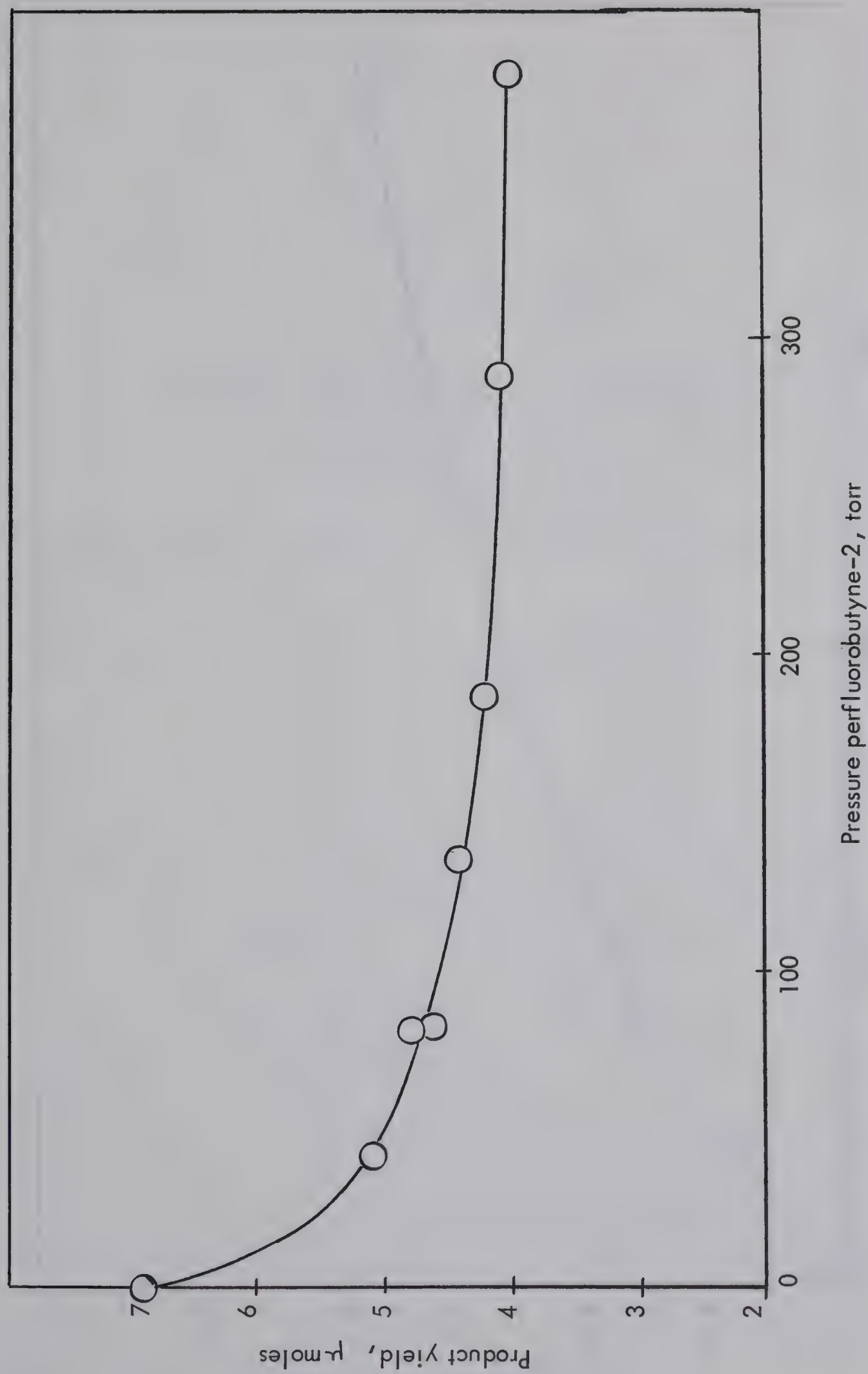


Fig. 55 CO formation as a function of perfluorobutylene-2 pressure

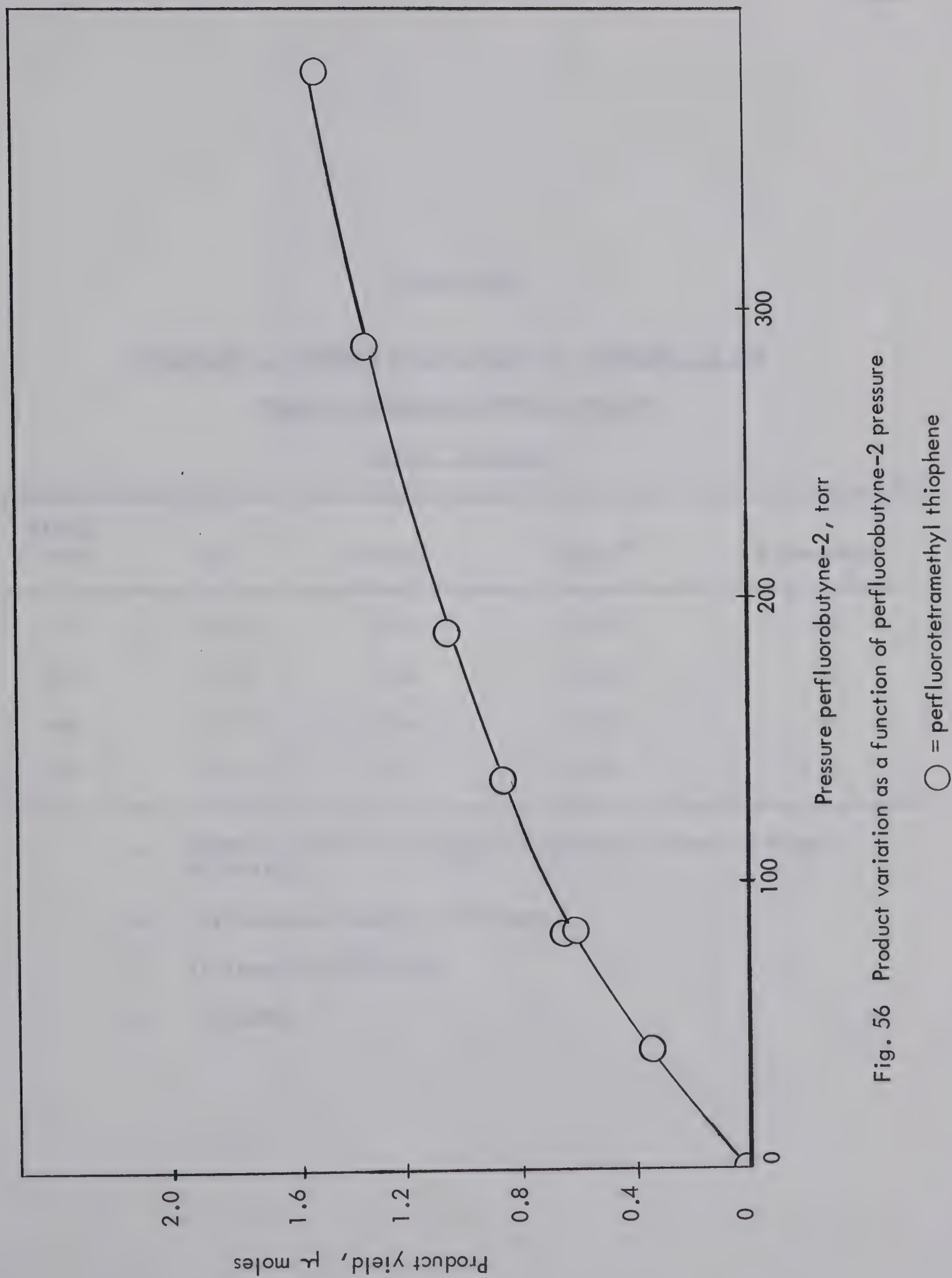


Fig. 56 Product variation as a function of perfluorobutylene-2 pressure

TABLE XXIII

VARIATION IN PRODUCT YIELDS WITH CO₂ PRESSURE IN THE
COS-CO₂-PERFLUOROBUTYNE-2 SYSTEM^a

Yield, μ moles

P(CO ₂) torr	CO	CO ^O -CO	C ₈ F ₁₂ S ^b	% Recovery ^c
0	3.98	2.98	1.50	50
251	3.78	3.18	1.33	42
560	3.70	3.26	1.32	41
950	3.69	3.27	1.26	39

a. P(COS) = 100 torr; P(C₄F₆) = 383 torr; Exposure time = 30.0 min.

b. Perfluorotetramethyl thiophene.

c. In terms of R^OCO-RCO.

d. Cd. Lamp.

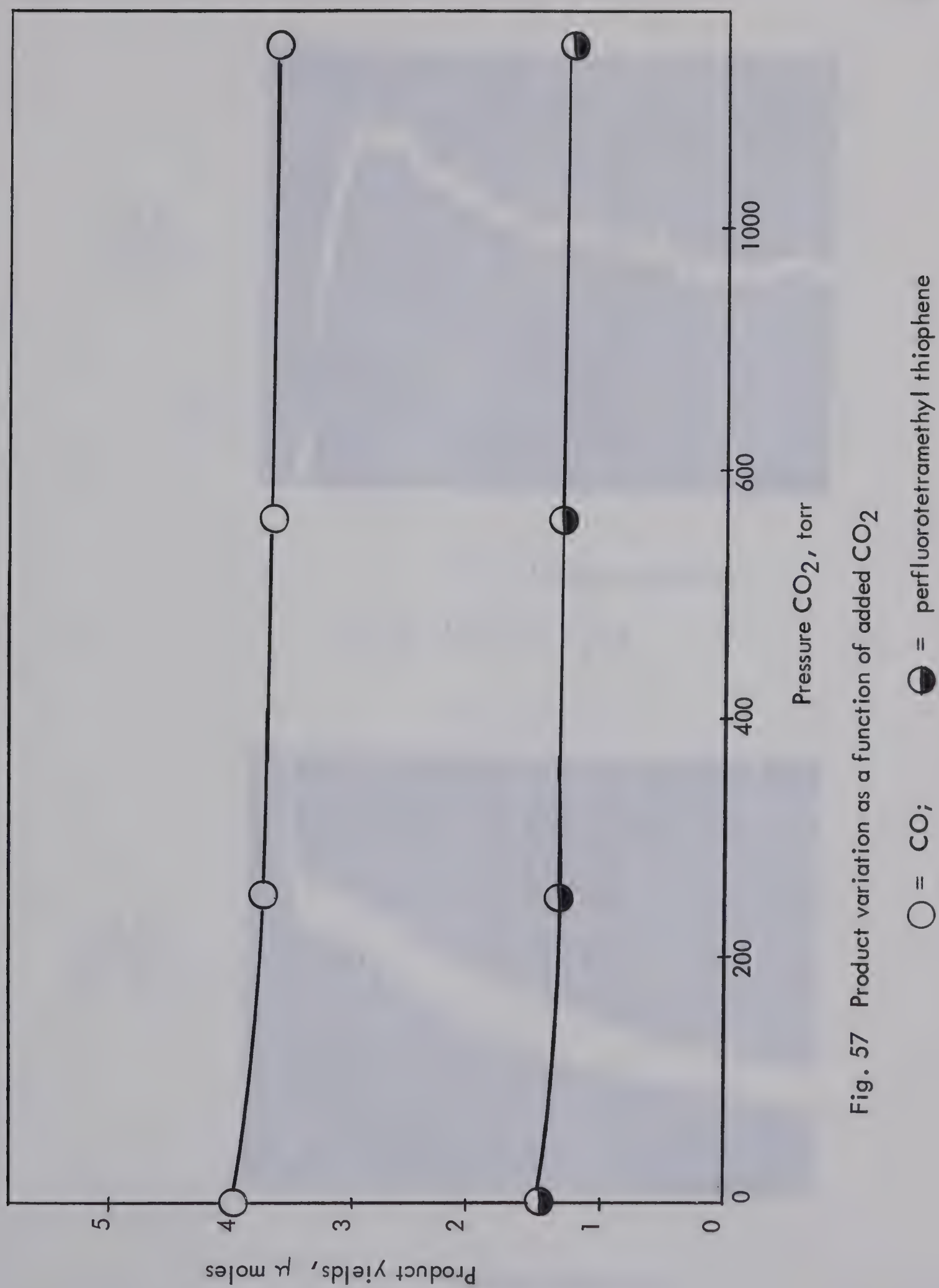
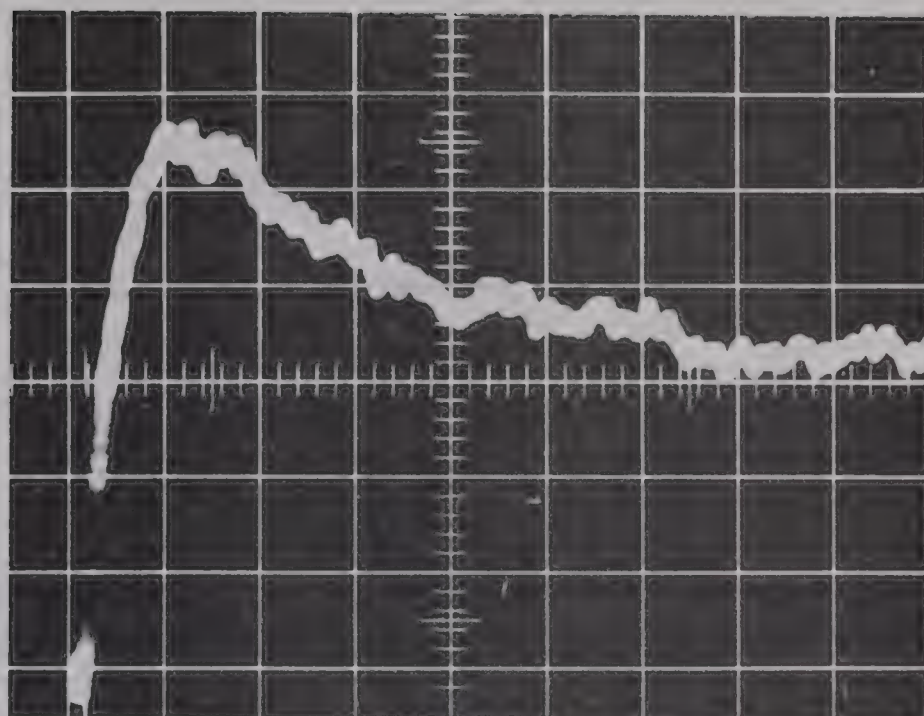


Fig. 57 Product variation as a function of added CO₂

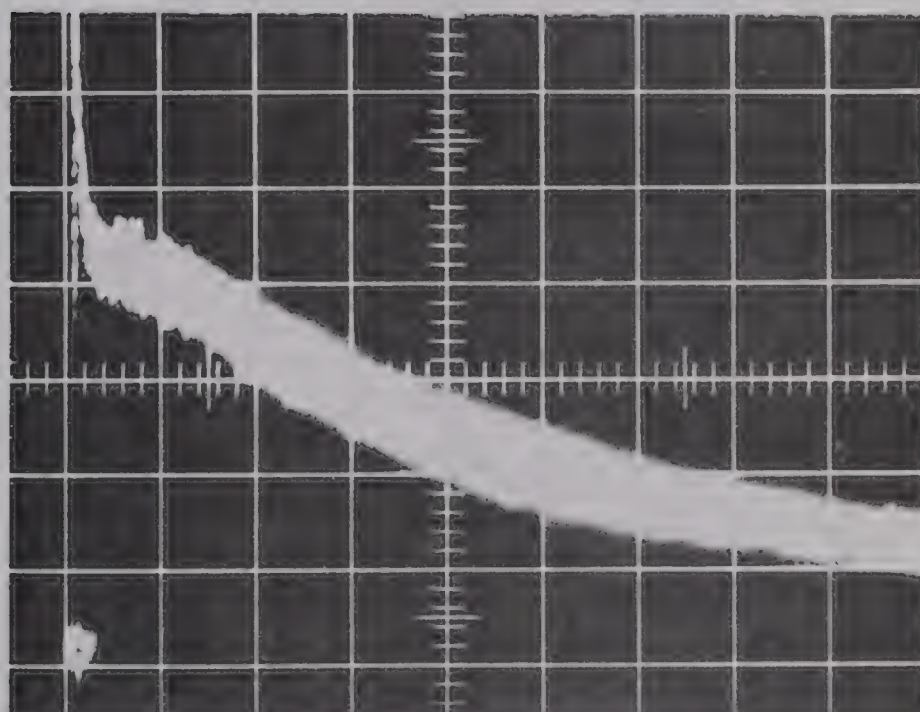
50.0
Millivolts
per div.



10.0 Milliseconds per div.

Fig. 58 Mass 194, C_4F_6S

50.0
Millivolts
per div.



0.5 Seconds per div.

Fig. 59 Mass 194, C_4F_6S

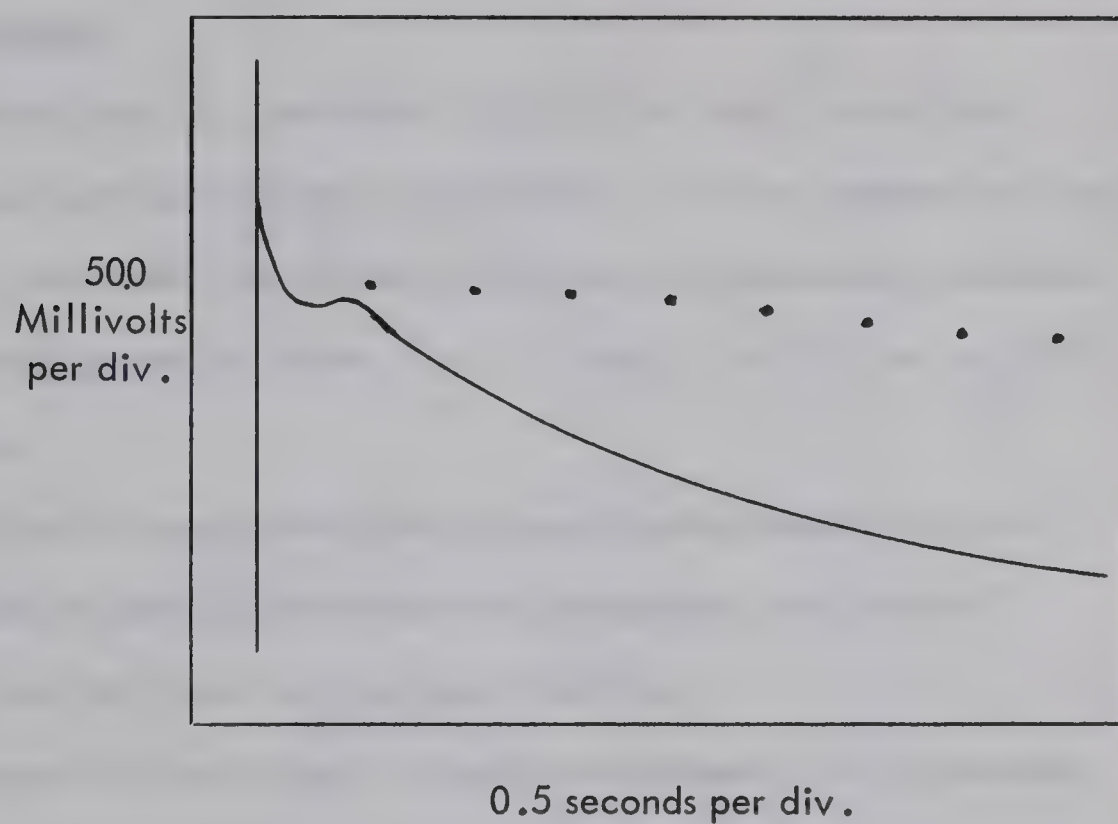


Fig. 60 Mass 194, C_4F_6S

Corrected for bleed-out

The signal strength is also reduced in the case of perfluorobutyne-2, the maximum signal being less than 500 millivolts.

MIXTURE OF ACETYLENE AND PERFLUOROBUTYNE-2

A. Static System

Photolysis of a mixture of COS (150 torr), acetylene (250 torr) and perfluorobutyne-2 (250 torr), in low conversion runs, was found to yield two gas chromatographically separable compounds having relative retention times 1.00 (I) and 3.30 (II) on an 8 ft. T.C.P. column.

Product I was identified by mass spectrometry and G.C. retention time as perfluorotetramethyl thiophene, the product obtained in the COS- perfluorobutyne-2 system.

Product II was shown by mass spectrometry to correspond to the compound $C_6H_2F_6S$ having molecular weight 220. N.M.R. analysis of this compound (Figure 61) indicated its structure to be that of 2,3-perfluorodimethyl thiophene. No other products were obtained in low conversion runs, the unsymmetrical perfluorodimethyl thiophene being the only cross product from the reaction of sulfur atoms with a mixture of acetylene and perfluorobutyne-2.

DISCUSSION

A. Nature of the Intermediate formed in the Reaction of Sulfur Atoms with the Triple Bond

Although no primary sulfur adduct was observed, in the static system, for the reaction of sulfur atoms with acetylenes

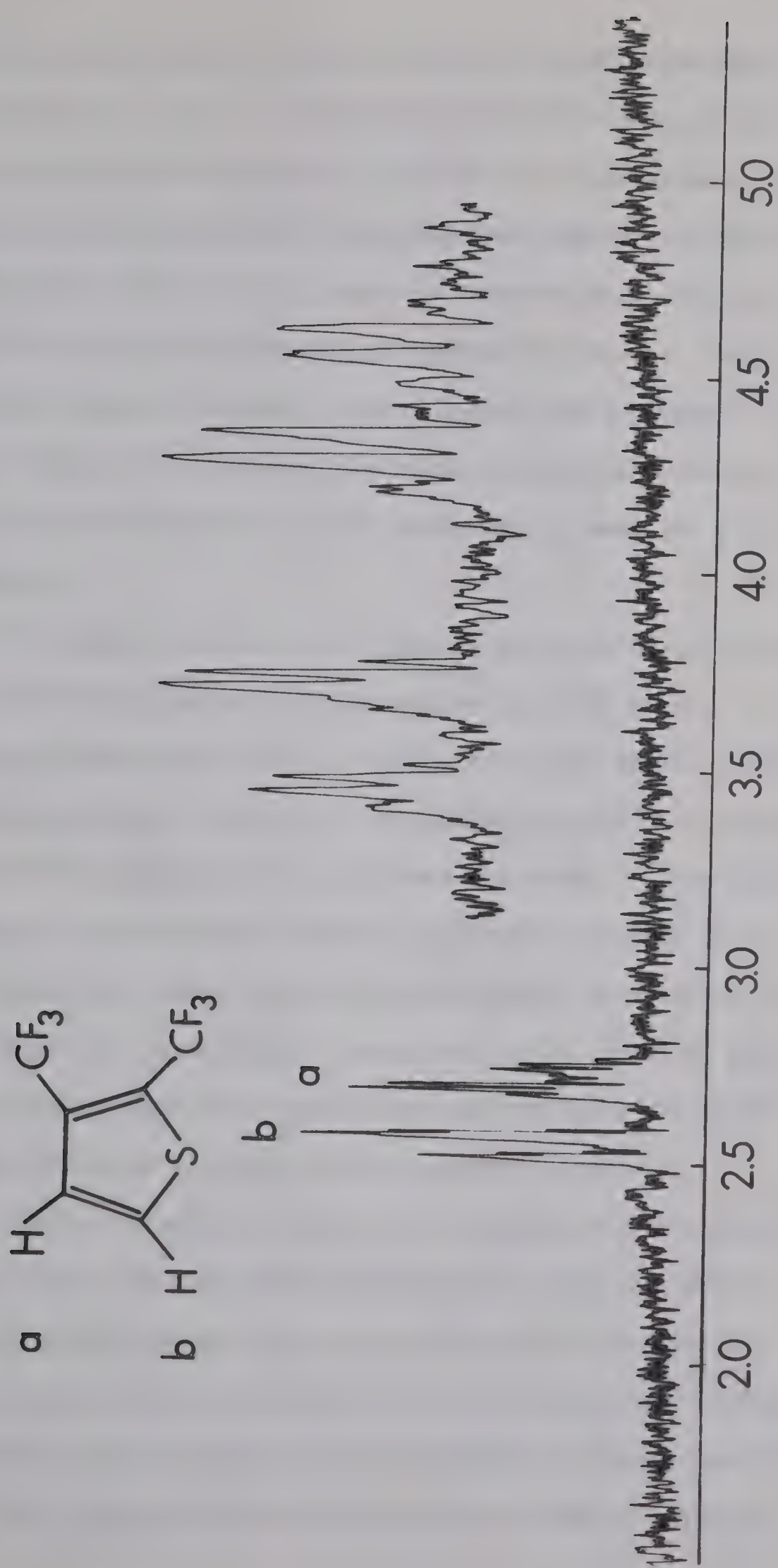


Fig. 61 Nuclear Magnetic Resonance Spectrum of 2, 3-perfluorodimethylthiophene.

these adducts were found by the technique of flash photolysis-kinetic mass spectrometry. In all cases the half-lives of the intermediates were in the range of seconds. Strong signals were observed for acetylene, methyl acetylene and dimethyl acetylene intermediates. The signal was found to increase with increasing methyl substitution indicating a greater reactivity resulting from the electron donating effect of the methyl groups. On the other hand perfluorination, producing a negative inductive effect, resulted in a much reduced reactivity as seen for perfluorobutyne-2.

To ensure that the above signals were not due to intermediates resulting from only C-H insertion of $S(^1D)$ atoms, ethylene episulfide was used as a source of sulfur atoms. Photolysis of ethylene episulfide results in production of only $S(^3P)$ atoms (108) and $S(^3P)$ atoms do not insert into C-H bonds. Flash Photolysis of ethylene episulfide with dimethyl acetylene resulted in a strong C_4H_6S signal which could result only from interaction of $S(^3P)$ with the triple bond. The signal C_4F_6S , obtained with perfluorobutyne-2 must also arise from reaction with the triple bond since C-F bonds are inert towards sulfur atoms.

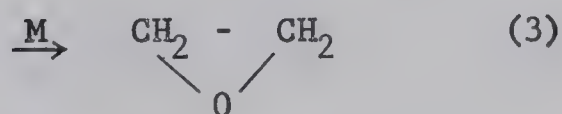
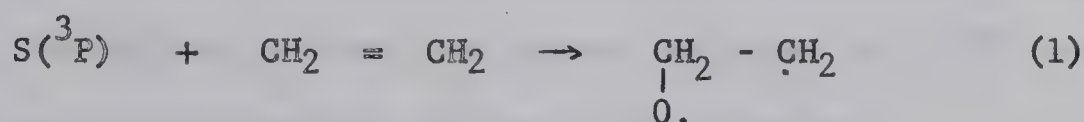
There are only two plausible structures for the sulfur-acetylene adduct; they are the thiacyclopropene and the thio-ketene. Thiacyclopropenes have never been isolated before and little is known about their stabilities or reactivities. Thioketene was reported by Howard (109) who stated that the monomer was stable at $-80^\circ C$ but upon warming, it polymerised to a white insoluble

solid. No direct evidence for the thioketene monomer was obtained although analysis of the polymer indicated that its precursor was probably thioketene. Since thiacyclopropene has never been reported its physical and chemical properties can only be estimated. Nelson and Jessup (81), taking the difference between the calculated and experimental heats of formation, have estimated the strain energies (s.e.) of cyclopropane, ethylene oxide and ethylene episulfide to be 25, 13 and 9 kcal./mole respectively. The difference in strain energy between cyclopropene and cyclopropane has been estimated to be (Δ s.e. ca. 27 kcal./mole) (110). If we assume the same energy difference (Δ s.e.) for oxirene and thiacyclopropene, we obtain strain energies of 40 and 36 kcal./mole respectively and s.e. for cyclopropene turns out to be 52 kcal./mole. On the basis of strain energy alone, thiacyclopropenes should be more stable than the corresponding cyclopropenes. This would mean that, since 1,2-dimethyl cyclopropene (117) is a stable compound at room temperature, the methylated thiacyclopropenes should also be stable at room temperature.

Cyclopropane has a larger strain energy than ethylene episulfide and yet cyclopropane is stable while ethylene episulfide undergoes a slow polymerisation reaction at room temperature. Strain energies alone, therefore, are not sufficient for predicting long term stability or chemical reactivity. Thiacyclopropenes may also undergo a similar polymerisation or follow some other decomposition path. Although ring strain may not predict the reactivity of a molecule it may be able to

furnish some information regarding the stability or degree of isomerisation of an initially produced adduct.

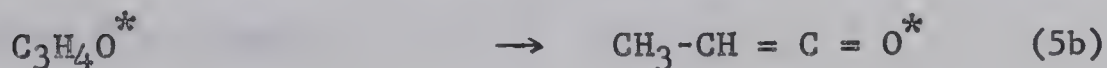
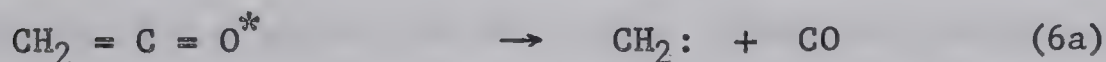
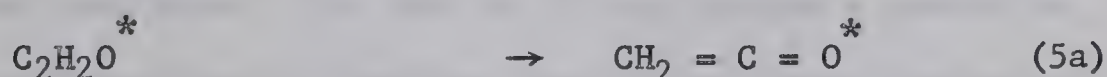
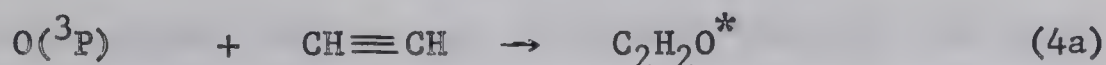
It is well known that addition of methylene (7) or $O(^3P)$ atoms (53) to ethylene results in extensive isomerisation and fragmentation. Methylene addition results in a pressure dependent ratio of cyclopropane/propylene, propylene resulting from isomerisation of the hot cyclopropane. Cvetanovic (53) has shown that addition of $O(^3P)$ to ethylene results in further reaction of the hot adduct



The addition of $S(^1D)$ to the double bond of ethylene is at least as exothermic as $O(^3P)$ addition and yet the only cyclic product formed in the reaction is ethylene episulfide (71). The strain energy of ethylene episulfide is only 4 kcal./mole less than for ethylene oxide and yet a drastically increased stability is observed in the initial adduct, ethylene episulfide. It is seen that the sulfur product is much more stable with respect to $S(^1D)$ addition than would be predicted and still, unlike ethylene oxide, ethylene episulfide is not stable at room temperature but tends towards polymerisation.

In light of the above observations, the possibility of thiacyclopropene formation, from the reaction of sulfur atoms with acetylene, will be discussed. Addition of a $S(^1D)$ atom to the triple bond of acetylene or a substituted acetylene should result in the initial formation of a hot thiacyclopropene molecule. This hot thiacyclopropene is then either stabilised or undergoes secondary reactions.

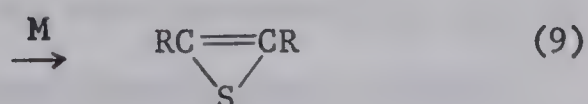
Arrington et al. (107) have investigated the reactions of $O(^3P)$ with acetylene and methyl acetylene and observed fragmentation of the initial adduct, but unlike addition of $O(^3P)$ to ethylene, no cyclic compound (oxirene) was obtained.



Since $S(^1D)$ addition to acetylene and methyl acetylene is at least as exothermic as $O(^3P)$ addition, a similar mode of fragmentation to CS and radicals might be expected. Flash photolysis of mixtures of COS with acetylene and dimethyl acetylene indicated that no CS was produced as a result of sulfur adduct

decompositions. Also careful product analysis of the COS-methyl acetylene static system indicated that no ethylene was formed thus eliminating the possibility of fragmentation of a methyl thioketene to CS and ethylidene. This data indicates that reactions similar to 6a and 6b do not occur in the corresponding $S(^1D)$ systems.

This increased stability towards fragmentation seems to be present in the COS-acetylene system, similar to that found for COS-ethylene. This does not necessarily mean, however, that the reaction stops after formation of the thiacyclopropene. Since ΔH_f of CS is less than ΔH_f of CO, reactions 6a and 6b for the sulfur product may be less favorable than for the analogous O atom reactions. The lack of CS and radicals cannot be taken as evidence that a reaction similar to 5a does not occur for the COS-acetylene system but only that a reaction similar to 6a does not. We are still left with the possibility that isomerization to the thioketene structure occurs and that the reaction then stops at this stage.

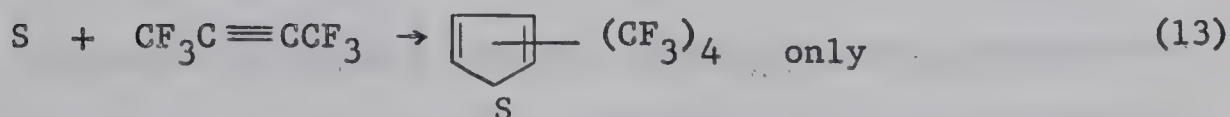
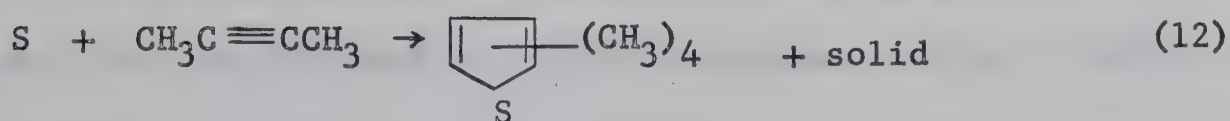
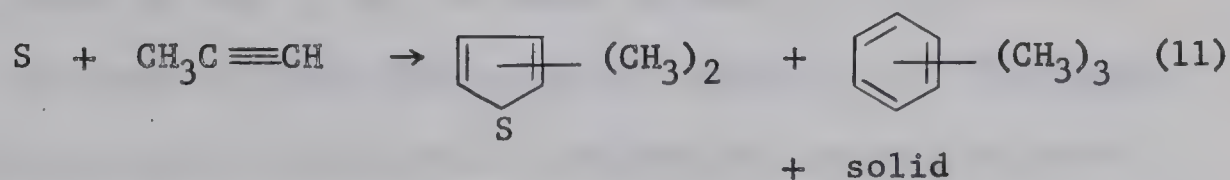


If a thiacyclopropene product is produced it must disappear by subsequent reaction or decomposition, as it is not found as a stable reaction product.

B. Reactivity of the Sulfur Intermediate Formed From the Reaction of S atoms With the Triple Bond.

From the flash photolysis-mass spectrometry it has been indicated that the addition product in the reaction of sulfur atoms with the triple bond is a sulfur adduct having either the thiacyclopropene or thioketene structure.

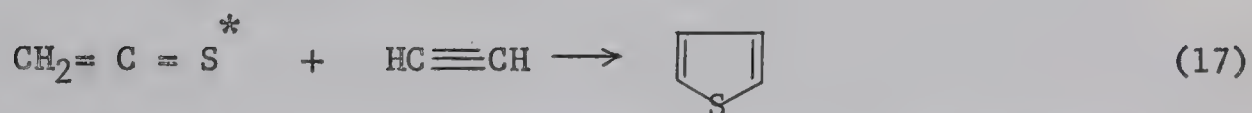
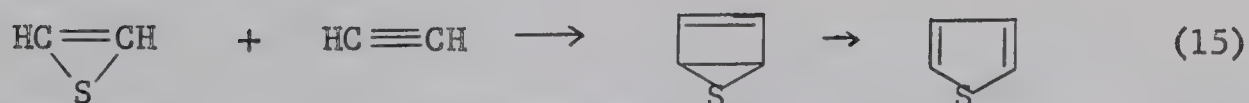
Stable products from the reactions of S atoms with acetylenes are represented by the following equations:



Yields of volatile products for the hydrocarbons were < 5% (solid is major product), while for perfluorobutyne-2 the perfluorotetramethyl thiophene represented ca. 50% of the sulfur atoms consumed.

Time resolved oscillograms for the COS-acetylene system (Fig. 41) shows that thiophene is formed readily while benzene (Fig 40) shows a strong delay in its formation. Thiophene is there-

fore formed by reaction of the C_2H_2S intermediate with a second acetylene molecule. The following reactions are possible:

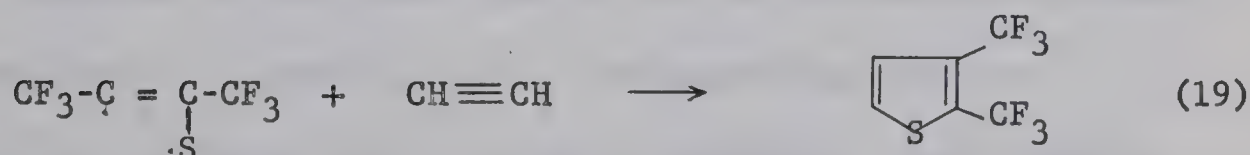
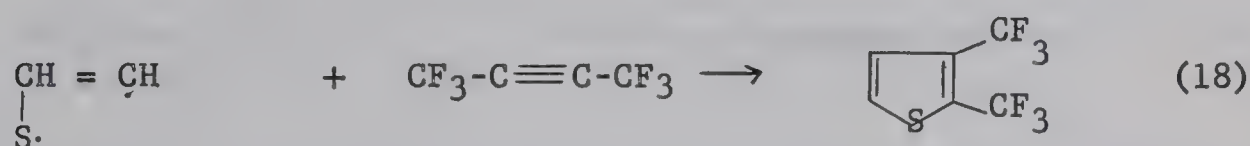


Reaction 14, 15 and 16 appear plausible, but it is difficult to envisage a transition state for reaction 17. Thiophenes therefore most likely result from reactions of a second molecule of substrate with the intermediate thiacyclopropene or its biradical form.

The major reaction of sulfur atoms with perfluorobutyne-2 leads to conversion to the corresponding thiophene, at high substrate pressures. Since isomerisation of the initial thiacyclopropene structure to the thioketene is rather unlikely, the reactive intermediate in this case is probably perfluorodimethyl thiacyclopropene or its biradical form.

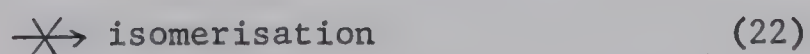
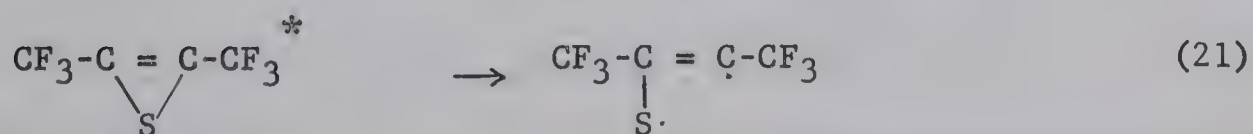
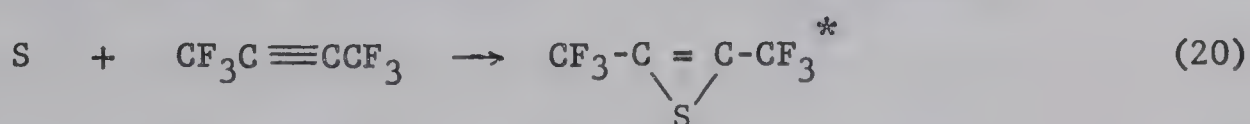
The reaction of sulfur atoms with a mixture of acetylene and perfluorobutyne-2 resulted in the formation of only one cross

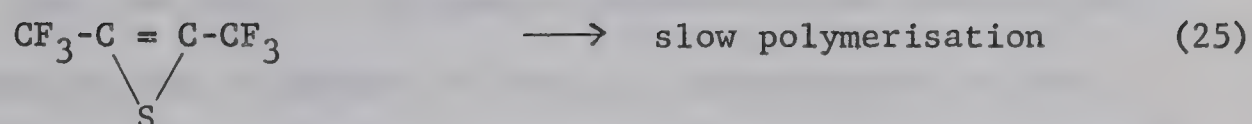
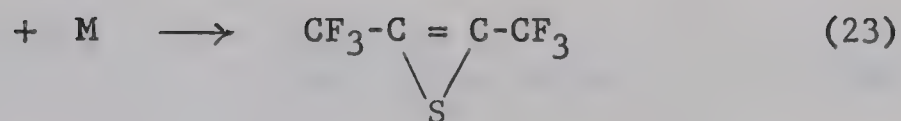
product. This product was 2,3-perfluorodimethyl thiophene, the unsymmetrical cross product. If thiophenes are formed by either reaction (14) or (15) a symmetrical thiophene should have been obtained. The formation of the unsymmetrical thiophene must therefore indicate that reaction (16) is the one responsible for thiophene formation.



In the mixed reaction it is not possible to determine whether both reactions (18) and (19) occur, or only one of them.

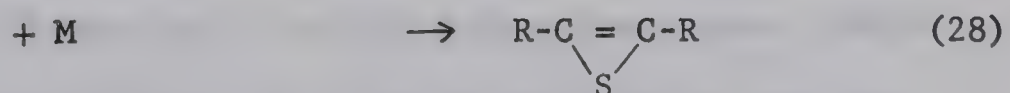
The large thiophene yield observed in the COS-perfluorobutyne-2 system may be due to the instability of the perfluorodimethyl thiacyclopropene, which opens to the biradical and can then react with substrate to form the corresponding thiophene. The large yield is probably also favored by the fact that the thiacyclopropene does not isomerise to the corresponding thioketene:





Addition of the inert gas CO_2 to the COS-perfluorobutyne-2 system resulted in a lowering of the corresponding thiophene yield. This could only be explained in terms of additional stabilisation of the intermediate thiacyclopropene structure (reaction 23) followed by a slow polymerisation of the thermalised perfluorodimethyl thiacyclopropene.

The general reaction scheme must contain the following reactions:





The low yield of thiophene products in the hydrocarbon systems must be due to either or both (a) isomerisation of the thiacyclopropene biradical to give the thioketene structure (which does not react to yield thiophenes but probably only polymerises) or (b) formation of stable thiacyclopropenes which disappear by some polymerisation reaction. Addition of large amounts of CO_2 to the COS-acetylene system did not increase the thiophene formation. Addition of the inert gas would be expected to decrease the isomerisation reaction and favor formation of the thiacyclopropene, thus suggesting that thermal thiacyclopropene does not react further to yield thiophene but probably just polymerises.

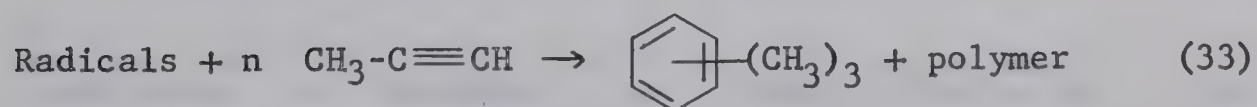
If isomerisation to the thioketene is the only factor responsible for the low thiophene yields, it follows that an increase in thiophene yield should be observed in going from acetylene to dimethyl acetylene, since methyl group migration should be slower than H atom migration. This increase was not observed suggesting again that formation of stable thiacyclopropenes (which probably only polymerise slowly) may also be responsible for the low thiophene yield.

C. Benzene Formation in the Reaction of Sulfur

Atoms with Acetylenes

The slow formation of benzene (Fig. 40) indicates that this product may not be formed in a primary reaction, resulting rather from some secondary process. The signal, shown in oscillogram 40, increases slowly over the entire range of 100 milliseconds and finally reaches a steady value beyond this period.

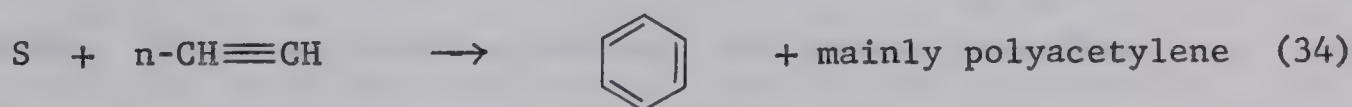
Additional evidence suggesting a secondary formation of benzene was obtained using a fast flow system. The products (including intermediate adducts) from the COS-acetylene system were trapped in liquid nitrogen at the exit end of a fast flow system. The excess COS and acetylene were then removed at -131°C ; the condensible products remained behind. Methyl acetylene was then added to these products at -131°C and the mixture was allowed to warm up slowly to room temperature. Product analysis showed that trimethyl benzene was the only product formed in this dark reaction. Its formation must be due to reaction of methyl acetylene with radicals or unstable intermediates of the COS-acetylene reaction. The following scheme is suggested to account for these observations:



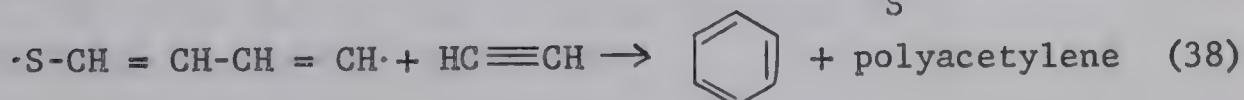
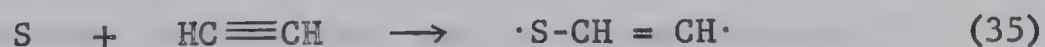
The trimethyl benzene could not have been produced by sulfur atoms produced in the dark reaction. If sulfur atoms were precursors to

the trimethyl benzene, dimethyl thiophene should also have been observed. It is also necessary to conclude that the benzene product was not formed by reaction of a C_2H_2S biradical, as this intermediate should also have resulted in the formation of methyl thiophene, contrary to our findings. Although secondary reactions appear to result in the formation of benzene compounds a second method of benzene formation should not be overlooked.

Benzene is always found as a small product in acetylene polymerisation reactions initiated by free radicals (105). In the COS-acetylene reaction the main product is a solid which resembles polyacetylene. It is reasonable then to expect that some benzene would also be formed in the S atom initiated polymerisation of acetylene.



A pressure study showed that at increasing pressures of acetylene the benzene yield increased from zero to a steady maximum value. At the same time the thiophene yield, with increasing acetylene pressure, rose to a maximum and then decreased to zero at high substrate pressures. This behavior would suggest a common precursor to the two products:



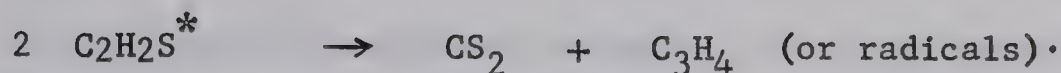
The decrease of thiophene and the increase of benzene with added acetylene may arise from a competition of the C_4H_4S radical between ring closure and further reaction with acetylene. Increasing amounts of acetylene would thus favor the addition reaction.

D. Carbon Disulfide Formation in the COS-Acetylene System.

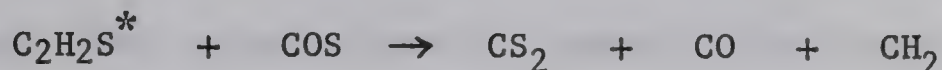
The major volatile sulfur containing compound formed in the reaction of sulfur atoms with acetylene was CS_2 ; yet even this product was formed in only small amounts. Figure 35 shows that the CS_2 formation is highest at low acetylene pressures and decreases with increasing pressure. Addition of a large amount of CO_2 to this system was also found to result in a decrease in the CS_2 formation. The above results indicate that carbon disulfide is formed from some hot precursor.

Flash photolysis of a mixture of COS and acetylene resulted in only CS_2 formation. The high intensity photolysis resulted in ca. 60% of the initial sulfur atoms being recovered as CS_2 . When the pressure of the same system was increased seven-fold, this value dropped to ca. 15% again indicating a pressure dependence on the CS_2 formation.

It is important to note that due to the negligible CS formation in these systems the CS_2 cannot result from a free CS precursor. Rather the pressure dependence and light intensity effect suggest that hot thiacyclopentene or thioketene molecules may be precursors to the CS_2 production.



A second possibility is the reaction of the hot $\text{C}_2\text{H}_2\text{S}$ with COS



A small amount of CS_2 is always formed in most COS-hydrocarbon systems. While its exact mode of formation has not yet been elucidated, it is thought to be due to secondary reactions or secondary photolysis.

Flash photolysis of COS-acetylene mixtures indicate that CS_2 is a primary product not arising from secondary photolysis.

E. Insertion Reactions

The reaction of $\text{S}(^1\text{D})$ atoms with acetylenes resulted in no stable mercaptan products. With methyl and dimethyl acetylenes no evidence for C-H insertion into the methyl groups was observed. This is an unusual observation in view of the C-H insertion reactions found for other hydrocarbon systems.

This may be due in part to the increased reactivity of the triple bond. For cis and trans-2-butenes approximately 30% of the sulfur atoms inserted into the methyl C-H bonds. With dimethyl acetylene an increased A factor for the addition reaction may result in less reactivity with the saturated part of the molecule. It is unlikely, however, that no insertion into the methyl group occurs. The lack of mercaptan formation is probably due to secondary reactions of the initial insertion product.

The C-H insertion product of methyl acetylene would be propargyl mercaptan. This compound has been prepared by Sato and Miyamoto (118) and is reported to be relatively stable at room temperature. The authors reported, however, that when distillation of the mercaptan was attempted at ordinary pressure it polymerised explosively. Insertion of $S(^1D)$ atoms into C-H bonds is ca. 85 kcal./mole exothermic. Absence of any stable mercaptan product may therefore be attributed to polymerisation or decomposition of the initially-formed hot mercaptan.

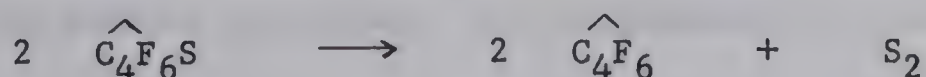
CHAPTER VII

SUMMARY AND CONCLUSIONS

Sulfur atoms react with cyclopentene to yield the episulfide, cyclopentene-3-thiol, cyclopentene-4-thiol and cyclopentene-1-thiol. Random insertion on the alkenylic positions was observed while the vinylic mercaptan, cyclopentene-1-thiol, was formed in only small quantities. Studies with added CO_2 indicated that triplet sulfur atoms react only by addition to the double bond resulting in episulfide formation. Triplet sulfur atoms are inert towards C-H bonds. An increase in the ratio $R(\text{mercaptan})/R(\text{episulfide})$ was observed with increasing translational energy of the sulfur atom.

The COS-cyclohexene system also yielded episulfide and two alkenylic mercaptans, cyclohexene-3-thiol and cyclohexene-4-thiol, formed by random insertion into the alkenylic C-H bonds. No vinylic mercaptan was formed in this system.

The behavior of the perfluoro olefin C_4F_6 reveals a drastic decrease in π -bond reactivity (with respect to sulfur atom addition) caused by the strong electron-withdrawing power of fluorine atoms. The product $\text{C}_4\text{F}_6\text{S}$ was observed by flash photolysis-kinetic mass spectrometry but the stability of the cyclo- C_4F_6 episulfide was found to be low, and its probable mode of decay is the bimolecular reaction:



Sulfur formation (elemental sulfur was the major reaction product) probably also resulted from third-body recombination of S atoms by $\hat{\text{C}}_4\text{F}_6$.

Insertion of $\text{S}(^1\text{D})$ atoms into methyl C-H bonds of trimethylethylene and tetramethylethylene was observed and compared to existing data for propylene, cis and trans-2-butenes and isobutylene. The series of methylated ethylenes showed that the rate of insertion per C-H bond was essentially constant for all members of the series. This indicated that the reactivity of $\text{S}(^1\text{D})$ atoms towards the double bond is essentially unaffected by the degree of substitution on the double bond. This is in contrast to the electrophilic behavior exhibited by $\text{S}(^3\text{P})$ atoms.

The COS-vinyl chloride system yielded episulfide as the major product (85% of the total volatile products) and a chloro mercaptan believed to be 2-chlorovinyl mercaptan (15%). Considerable polymerisation was observed in this system. Relative rate studies showed that vinyl chloride is 1.4 times more reactive than ethylene towards $\text{S}(^3\text{P})$ atom addition. This is attributed to the lower ionisation potential for vinyl chloride compared to ethylene, probably resulting in a lower activation energy for the addition reaction. The value of 1.4 is somewhat lower than would be predicted on the basis of ionisation potential alone and is probably due to the electron-withdrawing effect of the Cl atom.

The reaction of sulfur atoms with cis and trans-1,2-dichloroethenes resulted in polymerisation of the substrate with no volatile product formation. In the presence of a large excess

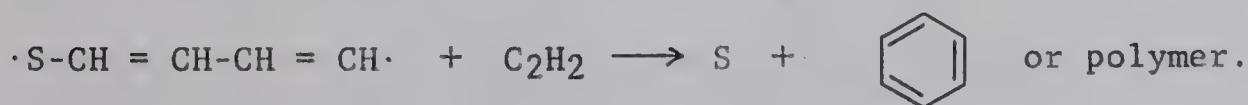
of CO_2 , episulfide formation was observed from addition of $\text{S}(^3\text{P})$ atoms to the double bond. Stereospecific addition of $\text{S}(^3\text{P})$ atoms to these two geometric isomers was observed; cis and trans-1,2-dichloroethenes yielded cis-episulfide (ca. 80%) and trans-episulfide (ca. 90%) respectively. Stereospecific addition arises from an increased barrier to rotation for the initially formed triplet biradical. This rotational barrier is probably largely due to spin interaction of the unpaired electrons of the biradical.

The reaction of sulfur atoms with alkyl chlorides resulted in C-H bond insertion only, forming vibrationally excited chloro mercaptans. Decomposition of the hot chloro mercaptans was observed; the stability of the initially-formed hot products increased with increasing molecular complexity of the alkyl chloride. Decomposition of the β -chloro mercaptans probably occurred by HCl elimination resulting in formation of cyclic episulfides. No insertion of $\text{S}(^1\text{D})$ atoms into C-Cl bonds was observed in these systems.

Possible transition complexes for the reactions of sulfur atoms were proposed. While insertion into alkenyl C-H bonds probably occurs from direct reaction with the C-H bond via a triangular transition complex, formation of vinylic mercaptans probably arises from isomerisation of hot singlet biradicals. Addition of $\text{S}(^3\text{P})$ atoms to the double bond indicate formation of a charge-transfer complex in the transition state, but, due to observed steric hindrance upon alkyl substitution, the transition

state probably resembles a σ -complex with formation of an incipient C...S bond. Addition of $S(^1D)$ to the double bond may result in formation of an initial singlet biradical rather than direct insertion into the π -bond with simultaneous formation of two C-S bonds. Stereospecific addition of $S(^1D)$ to the double bond does not require simultaneous bond formation.

A general reaction observed for the reaction of sulfur atoms with acetylenes was a sulfur atom initiated polymerisation of the substrate. Small yields of thiophenes and benzenes were observed (less than 5% of the sulfur atoms consumed). The general features of the system are illustrated by the following reactions:



Short-lived primary sulfur adducts of the alkynes were observed by the technique of flash photolysis-kinetic mass spectrometry. Their structures are either that of the corresponding thia-cyclopropenes or the thioketenes, but, due to their instabilities exact structural assignments could not be made.

The reactions of sulfur atoms with perfluorobutyne-2 resulted in a high conversion to perfluorotetramethyl thiophene (50% in terms of sulfur atoms consumed).

No insertion products were observed in the COS-alkyne systems due to decomposition or further reaction of the initially-formed products.

APPENDIX A

Mass Spectral Data

The following mass spectra were obtained on a Metropolitan-Vickers Model MS-2 mass spectrometer operated at 70 ev. All samples were transferred under vacuum into break seals after being removed directly from the reaction vessel or purified by gas chromatography.

MS-1: cyclopentene-1-thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
27	6.9	50	15.5
28	14.4	65	15.3
30	6.2	66	35.8
39	18.8	67	<u>100.0</u>
40	5.2	68	10.2
41	18.8	85	6.9
45	7.3	100 p	10.6
47	13.0		

MS-2: cyclopentene-3-thiol
+ cyclopentene-4-thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
27	8.3	65	29.7
39	30.8	66	39.7
40	8.5	67	<u>100.0</u>
41	31.2	68	6.0
45	14.7	85	5.4
47	6.8	100 p	8.1
55	5.3		

MS-3: cyclopentene episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
27	8.6	66	29.6
39	28.8	67	<u>100.0</u>
40	7.7	68	9.5
41	30.4	85	15.9
45	14.2	100 p	27.3
65	18.4		

MS-4: cyclohexene-3-thiol
+ cyclohexene-4-thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
26	10.6	53	20.2
27	47.8	54	77.5
29	18.2	55	21.2
31	16.0	65	11.7
39	70.3	67	<u>100.0</u>
40	12.8	73	13.8
41	73.5	77	21.2
42	28.7	79	39.4
43	27.6	80	22.4
45	26.6	81	37.2
47	39.4	82	37.2
50	10.6	114 p	17.0
51	20.2		

MS-5: cyclohexene episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
27	36.6	60	12.9
28	53.9	65	10.8
39	64.5	67	<u>100.0</u>
41	60.5	77	12.5
45	16.3	79	18.7
51	13.5	80	26.4
53	24.4	81	43.1
54	84.7	82	37.0
55	12.9	114 p	21.8

MS-6: 2,3-dimethyl-2-butene-1-thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
27	21.6	45	31.1	73	11.3
29	41.2	47	14.6	74	27.8
31	47.2	53	17.4	77	18.5
33	19.2	55	43.6	83	12.7
34	47.5	56	12.8	84	44.2
39	65.5	57	15.1	85	12.0
40	12.9	59	58.3	97	13.4
41	37.6	67	31.8	111	52.5
42	19.5	69	<u>100.0</u>	116 p	11.0
43	54.1				

MS-7: Tetramethylethylene episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
27	15.5	60	13.7
29	11.6	61	10.1
39	35.4	67	12.9
41	88.5	69	27.6
43	21.8	74	76.3
55	26.8	84	11.6
57	21.2	116 p	43.2
59	<u>100.0</u>		

MS-8: Trimethylethylene episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
27	33.2	59	26.2
29	19.0	60	25.0
39	45.0	61	17.8
41	<u>100.0</u>	67	11.6
42	14.2	69	45.0
45	35.5	70	13.6
47	13.5	74	70.5
53	29.0	83	16.5
55	35.5	87	17.6
58	10.2	102 p	77.5

MS-9: Trimethylethylene mercaptans, 2 and 3

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
27	38.8	60	19.6
29	21.9	61	16.8
39	50.6	67	16.0
41	50.6	69	42.1
42	20.2	70	22.3
43	52.2	71	22.4
45	46.1	74	50.6
53	29.2	87	14.6
55	44.4	97	17.4
59	<u>100.0</u>	102 p	60.6

MS-10: Trans-1,2-dichloroethylene episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
26	8.9	79	12.6
45	<u>100.0</u>	92	7.1
47	8.0	93	31.5
49	7.3	95	12.5
57	24.1	128 p	36.5
58	19.8	130 i	25.5
61	7.8		

MS-11: Cis-1,2-dichloroethylene episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
26	7.0	79	14.1
45	<u>100.0</u>	81	6.0
47	6.2	92	6.5
49	4.1	93	30.2
57	23.8	95	11.1
58	21.7	128 p	39.1
61	7.4	130 i	24.2

MS-12: Vinyl chloride episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
26	11.4	59	56.7
27	16.1	60	7.5
45	<u>100.0</u>	61	5.8
47	7.2	62	5.8
57	16.1	94 p	62.9
58	45.6	96 i	22.8

MS-13: 2-chloro-2-methylpropane-1-thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
27	28.1	53	21.0
28	12.6	54	43.7
29	28.4	55	98.0
36	16.2	56	13.5
38	12.7	58	6.6
39	63.5	59	22.0
41	62.1	60	24.0
42	7.1	67	15.1
43	11.2	73	32.6
45	56.9	77	29.4
46	25.7	79	11.1
47	28.8	88	<u>100.0</u>
48	14.4	124 p	10.7
49	6.1	126 i	3.5

MS-14: 2,3-perfluorodimethyl thiophene

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
31	3.9	113	3.0
44	20.4	132	4.4
45	10.0	151	28.4
57	5.2	170	29.6
58	5.2	201	62.5
69	21.8	220 p	<u>100.0</u>
82	4.8		

MS-15: Perfluorotetramethylythiophene

<u>m/e</u>	<u>Rel. Int.</u>	<u>Assignment</u>
31	1.8	CF
63	8.2	SCF
69	3.2	CF ₃
87	7.9	SC ₃ F
93	7.8	C ₃ F ₃
94	2.9	SC ₂ F ₂
99	4.0	SC ₄ F
106	8.0	SC ₃ F ₂
111	1.7	SC ₅ F
125	1.7	SC ₃ F ₃
130	3.0	SC ₅ F ₂
131	2.6	C ₃ F ₅
137	1.9	SC ₄ F ₃
143	3.5	C ₄ F ₅
149	2.1	SC ₅ F ₃

MS-15: Perfluorotetramethylythiophene

(continued)

<u>m/e</u>	<u>Rel. Int.</u>	<u>Assignment</u>
155	2.1	C ₅ F ₅
181	2.3	C ₄ F ₇
193	2.1	C ₅ F ₇
199	17.3	SC ₆ F ₅
218	2.9	SC ₆ F ₆
237	29.0	SC ₆ F ₇
243	2.6	C ₆ F ₁₁
255	3.2	C ₇ F ₉
268	4.4	SC ₇ F ₈
287	<u>100.0</u>	SC ₇ F ₉
305	17.3	C ₈ F ₁₁
337	96.6	SC ₈ F ₁₁
356	58.5 p	SC ₈ F ₁₂
357	5.8 i	SC ₈ F ₁₂

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The Reactions of Sulfur Atoms.

VIII. Further Investigation of the Reactions with Olefins. Relative Rates of Addition of Sulfur (3P) and (1D) Atoms

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Abstract: The reactions of S atoms with cyclic olefins, chlorinated and methyl-substituted ethylenes, and perfluorocyclobutene have been examined. The salient features of these reactions are similar to those already reported for other olefins. From rate measurements, it is concluded that episulfides arise from $S(^1D)$ as well as $S(^3P)$ atom addition to olefins and that the fraction of sulfur atoms, from the photolysis of COS, reacting in the triplet state is less than 0.3. Relative rate constants have been obtained for the addition of $S(^1D)$ and $S(^3P)$ atoms to a representative series of olefins. The electrophilic character of $S(^3P)$ atoms clearly manifests itself in the trend of reactivity with olefin structure. Singlet atoms are probably also electrophilic, but they are generally less selective than triplet.

The reactions of sulfur atoms with ethylene, propylene, 1-butene, isobutylene, 1,3-butadiene, *cis*- and *trans*-2-butene, and 1,1-difluoroethylene have been reported.¹ Episulfides and vinylic and alkenyl-type

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mercaptans are the principal products of electronically excited $S(^1D)$ -atom reactions, while ground-state triplet atoms afford only episulfides. The alkenyl-type mercaptans form in a random insertive reaction into the C-H bonds of the olefin, while the vinylic-type mercaptan formation may equally well be envisaged from double-bond addition, through isomerization of the energy-rich episulfide biradical intermediate.^{1c,2}

(2) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4**, 142 (1966).

With *cis*- and *trans*-2-butene, the episulfide-forming reaction is stereospecific not only with $S(^1D)$, but also with $S(^3P)$ atoms. Consequently the extent of triplet S-atom participation in COS-2-butene systems cannot be estimated from the product geometry.

The objectives of the present investigation were two fold: (a) to extend our studies on the effects of substituents and structural changes in the parent olefin molecule on the nature of the reaction and its products, and (b) to establish the order of reactivity of triplet- and singlet-state atoms as a function of structural parameters for a representative series of olefins.

Experimental Section

The photolysis assembly and product-handling procedures were essentially the same as in the previous studies on S-atom reactions. Materials were the best available grade. Product analyses were carried out by gas chromatography on the low-temperature condensates.

Results

Cyclopentene. The condensable fraction of the reaction products was found to consist of three gas chromatographically separable components (I-III). According to their mass spectra, shown in Table I, all three are isomers of empirical formula C_5H_8S . I and II were formed in sufficient amounts to enable identification by nmr spectroscopy. The major product (II) is the episulfide. The nmr spectrum of I consisted of two sets of doublets centered at τ 8.39 and 8.57 and two singlets at τ 4.28 and 4.34. The doublet absorptions occur in the region to be expected for thiol protons, and the singlets are probably due to vinylic protons. Therefore I actually consists of two isomers and these are probably alkenyl mercaptans, cyclopentene-3-thiol and cyclopentene-4-thiol. Intensity considerations showed that the concentration ratio of the two isomers was *ca.* 2:1, but it could not be determined which was present in the larger yield. The only structure possible for product III is that corresponding to cyclopentene-1-thiol. Its retention time corresponded to that of an authentic sample.³

(3) D. C. Sen, *J. Indian Chem. Soc.*, **13**, 268 (1936).

The COS-cyclopentene system was examined as a function of cyclopentene pressure, and added CO_2 pressure, exposure time, and wavelength of radiation. Figure 1 shows rates of product formation as a function of cyclopentene pressure. At pressures >200 torr the rate is constant and $R(\text{mercaptan})/R(\text{episulfide})$, $(R(M)/R(E))$, has a limiting value of 0.80. At the highest pressure used (300 torr) $R(CO)$ is nearly equal to $R^0(CO)/2$. With increasing exposure time, the onset of secondary reactions and the attenuation of incident light intensity due to polymer deposition result in a decrease in the rate, but $R(M)/R(E)$ remains approximately constant.

Table I. Mass Spectra of Products from the Reactions of Sulfur Atoms with Cyclopentene, Cyclohexene, Trimethylethylene, Tetramethylethylene, Vinyl Chloride, and *trans*-1,2-Dichloroethylene^a

M/e	Cyclo- pentene- 1-thiol	Cyclo- pentene- 3-thiol + -4-thiol	Cyclo- pentene episulfide	Cyclo- hexene- 3-thiol + -4-thiol	Cyclo- hexene episulfide	Trimethyl- ethylene episulfide	Tetra- methyl- ethylene mercaptan	Tetra- methyl- ethylene episulfide	Vinyl chloride episulfide	<i>trans</i> -1,2- Dichloro- ethylene episulfide
26				10.6					11.4	8.9
27	6.9	8.3	8.6	47.8	36.6	33.2	21.6	15.5	16.1	
28	14.4				53.9					
29				18.2		19.0	41.2	11.6		
31				16.0			47.2			
33							19.2			
34							47.5			
39	18.8	30.8	28.8	70.3	64.5	45.0	65.5	35.4		
40	5.2	8.5	7.7	12.8			12.9			
41	18.8	31.2	30.4	73.5	60.5	100.0	37.6	88.5		
42				28.7		14.2	19.5			
43				27.6			54.1	21.8		
45	7.3	14.7	14.2	26.6	16.3	35.5	31.1		100.0	100.0
47	13.0	6.8		39.4		13.5	14.6		7.2	8.0
49										72.7
50	15.5			10.6						
51				20.2	13.5					
53				20.2	24.4	29.0	17.4			
54				77.5	84.7					
55		5.3		21.2	12.9	35.5	43.6	26.8		
56							12.8			
57							15.1	21.2	16.1	24.1
58						10.2			45.6	19.7
59						26.2	58.3	100.0	56.7	
60					12.9	25.0		13.7	7.5	
61						17.8		10.1	5.8	7.8
62									5.8	
65	15.3	29.7	18.4	11.7	10.8					
66	35.8	39.7	29.6							
67	100.0	100.0	100.0	100.0	100.0	11.6	31.8	12.9		
68	10.2	6.0	9.5							
69						45.0	100.0	27.6		
70						13.6				
73				13.8			11.3			
74						70.5	27.8	76.3		
77				21.2	12.5		18.5			
79				39.4	18.7					12.6
80				22.4	26.4					
81				37.2	43.1					
82				37.2	37.0					
83						16.5	12.7			
84							44.2	11.6		
85	6.9	5.4	15.9				12.0			
87						17.6				
92										7.1
93										31.5
94									62.9	
95										12.5
96									22.8	
97							13.4			
100	10.6	8.1	27.3							
102						77.5				
111							52.5			
114				17.0	21.8					
116							11.0	43.2		
128										36.5
130										25.5

^a The spectra were obtained on a Metropolitan-Vickers Model MS-2 spectrometer at 70 ev.

The effect of added CO₂ on a reaction mixture consisting of 100 torr of COS and 51 torr of cyclopentene is shown in Figure 2. $R(M)/R(E)$ decreases from an initial value of 0.44 to 0.03 in the presence of 1250 torr of CO₂. Product recoveries, in terms of $R(CO)-R^{\circ}(CO)/2$ were independent of CO₂ pressure, indicating efficient stabilization of the initially formed "hot" episulfide even at low pressures.

The effect of wavelength of the exciting radiation was examined using a mixture consisting of 100 torr of COS and 250 torr of cyclopentene. The effective radiation of a medium-pressure mercury arc in the photolysis of COS is 2490 Å; under these conditions $R(M)/R(E) = 0.8$. Using the 2288-Å resonance line from a cadmium lamp, the ratio becomes 0.9.

Cyclohexene. The sulfur-containing products were resolved by gc into two peaks (I and II). II was identified as the episulfide by comparison of the nmr and mass spectra with those of an authentic sample. The nmr spectrum of I indicated that two isomeric alkenyl mercaptans were present in approximately equal proportions; they are probably cyclohexene-4-thiol and cyclohexene-3-thiol. At 2490 Å, $R(M)/R(E) = 0.8$ for a mixture consisting of 100 torr of COS and 76 torr of cyclohexene. The extrapolated value in the complete pressure stabilization region is *ca.* 1.0. The addition of CO₂ also suppresses mercaptan formation and enhances the episulfide yields.

Perfluorocyclobutene. Photolysis of COS-perfluorocyclobutene mixtures at 2288 Å yielded CO, and a solid deposited on the walls of the reaction vessel. Oxidation of the solid gave SO₂ and smaller amounts of CO₂ indicating a slow reaction between S atoms and perfluorocyclobutene. The perfluorocyclobutene episulfide product could indeed be detected in flash photolysis (400 μ of COS and 800 μ of cyclo-C₄F₆) by kinetic mass spectrometry.⁴ It appears to be unstable at room

(4) W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **88**, 4277 (1966); W. K. Dinkel, R. Messmer, P. Kebarle, O. P. Strausz, and H. E. Gunning, to be published.

temperature, undergoing decomposition with a half-life of the order of minutes.

The rate of CO formation in the static experiments decreases with increasing pressure of cyclo-C₄F₆ (Figure 3a) and approaches $R^{\circ}(\text{CO})/2$ for a mixture consisting of 100 torr of COS and over 1000 torr of cyclo-C₄F₆.

When cyclo-C₄F₆ was added in increasing amounts to a mixture of 100 torr of COS and 75 torr of cyclopentene, no suppression of the cyclopentene reaction resulted up to 500 torr of cyclo-C₄F₆ (Figure 3b) although the ratio of mercaptan to episulfide was diminished considerably.

From comparison of the data in Figures 1–3 it is concluded that the reactivity of cyclo-C₄F₆ with S atoms is less than one-tenth of that of cyclopentene, but cyclo-C₄F₆ and CO₂ are about equally efficient in promoting the electronic relaxation of S(¹D) atoms



Trimethylethylene. In low-conversion runs, four gas chromatographically separable sulfur-containing products were formed. All of them were isomers with molecular weight 102 (C₅H₁₀S). Upon addition of CO₂ to the system, one was formed in increasing amounts, at the expense of the other three, and therefore it has been identified as the episulfide. The remaining ones are probably isomeric alkenyl mercaptans. In a mixture consisting of 100 torr of COS and 300 torr of trimethylethylene, $R(M)/R(E)$ was found to be 0.73 at 2490 Å.

Ad#

Tetramethylethylene. A gc analysis of the condensable fraction showed two reaction products; both had molecular weights of 116 ($C_6H_{12}S$). Identification of one of them as the episulfide was made in a manner similar to that used for trimethylethylene. Tetramethylethylene episulfide is an unstable compound and decomposes readily (on the gc column) to yield tetramethylethylene and sulfur. In a mixture of 100 torr of COS and 125 torr of tetramethylethylene, $R(M)/R(E)$ was 0.73 at 2490 Å.

Vinyl Chloride. The COS-vinyl chloride system yielded two products. Both had molecular weights of 94 (C_2H_3ClS). One was identified by nmr spectroscopy as the episulfide. The nmr spectrum of the other was consistent with a chlorovinyl mercaptan structure, but insufficient amounts were formed to determine whether it is the *cis* or *trans* isomer, or a mixture of both. The effect of increasing pressure of vinyl chloride on the rates at a constant pressure of COS (100 torr) is shown in Figure 4; photolyses were performed at 2288 Å. The general features of the reaction are consistent with those observed in other COS-olefin systems, except that at the highest pressure used (772 torr), $R(CO)$ is slightly less than $R^0(CO)/2$; this is probably due to competitive absorption by vinyl chloride. $R(M)/R(E)$ is also pressure dependent and reaches a limiting value of 0.19 at 600 torr of vinyl chloride.

***trans*-1,2-Dichloroethene.** Photolysis of COS-*trans*-1,2-dichloroethene mixtures using the 2490 Å source at moderate total pressures resulted in the formation of CO and a dark brown polymeric deposit. No volatile sulfur-containing products were found. In flash photolysis, however, the addition product with empirical formula of $C_2H_2Cl_2S$ could be detected by kinetic mass spectrometry, in relatively large yields. Therefore the static experiments were repeated with an excess of added CO_2 , under which conditions a condensable product was isolated and resolved by gc into two components. Both compounds were shown by mass spectral analysis to correspond to the formula $C_2H_2Cl_2S$. Since episulfides are the only major products arising from the photolysis of COS- CO_2 -olefin systems, they can only be geometrical isomers of the episulfide of 1,2-dichloroethene. By analogy with the results obtained in the COS- CO_2 -*cis*-1,2-dichloroethene (*vide infra*) and the COS- CO_2 -2-butene systems,^{1c} the *trans*-episulfide represented ca. 90% of the total products (as compared to 98% in the COS- CO_2 -*trans*-2-butene system^{1c}). Product yields, calculated in terms of $R(CO)-R^0(CO)/2$, increased with CO_2 pressure up to ca. 80%.

***cis*-1,2-Dichloroethene.** Condensable products were not observed unless a large excess of CO_2 was present. Experiments were performed using the Hg-arc source. Two products were formed, which eluted on the gc column at the same time as those formed in the COS- CO_2 -*trans*-1,2-dichloroethene system, and by similar reasoning the component, which represented 80% of the total, was taken to be the *cis* and the other the *trans* isomer. Product yields were ca. 10-20% at high pressures of CO_2 .

bf

Relative Rates of Addition of $S(^3P)$ Atoms. Relative rates were determined in competitive systems where olefin pairs were chosen such that they could be recovered from the reaction mixture by low-temperature distillation. All experiments were done with the Hg-arc source. Total olefin pressures did not exceed 60 torr; COS and CO_2 pressures were *ca.* 30 and 1250 torr, respectively. Under these conditions mercaptans were formed in trace quantities only. Rates for formation of episulfides were determined as a function of exposure time. Yields, calculated in terms of $R^0(CO)-R(CO)$, were in the range of 80–90% except in the case of C_5 olefins where they were *ca.* 60%. At least six runs were performed for each olefin pair at various exposure times. The results obtained for ethylene, propylene, 1-butene, isobutylene, *trans*-2-butene, *cis*-2-butene, 1-pentene, 2-methyl-1-butene, cyclopentene, and vinyl chloride are given in Table II. Although the conversions were kept as short as possible, secondary decompositions could not be entirely prevented; this is evidenced by the small positive intercept shown by the representative plot in Figure 5. In the least-mean-squares calculation of the rate constants, the origin was weighted twice to give a zero intercept (broken line, Figure 5). The error in the analytical data is believed not to exceed $\pm 10\%$.

Table II. Relative Rate Data for the Addition of $S(^3P)$ Atoms to Olefins

Olefin pair	Pressure, torr			k_2/k_1^a	% yield ^b
	Olefin	COS	CO_2		
(1) Ethylene	32.5	32.5	1256	6.9	85
(2) Propylene	11.5				
(1) Propylene	26.0	30.0	1262		
(2) Isobutylene	19.0			7.2	86
(1) Propylene	(I) 25.5	31.5	1223		
	(II) 44.7	32.2	1244	(I) 3.4	75
(2) <i>trans</i> -2-Butene	(I) 18.0	31.5	1223	(II) 2.3	77
	(II) 17.0	32.2	1244		
(1) <i>trans</i> -2-Butene	23.5	33.0	1317		
				0.48	83
(2) 1-Butene	24.4				
(1) Propylene	44.7	32.5	1231		
(2) <i>cis</i> -2-Butene	23.0			2.3	87
(1) <i>cis</i> -2-Butene	67.0	32.0	1217		
(2) 2-Methyl-1-butene	8.20			3.5	83
(1) 1-Pentene	64.0	31.5	1250		
(2) 2-Methyl-1-butene	10.7			5.8	63
(1) 1-Pentene	23.0				
(2) Cyclopentene	24.0	31.5	1250	1.9	54
(1) Vinyl chloride	150	100	1190		
(2) Propylene	30			4.8	77

^a $k_2/k_1 = k(S + \text{olefin (2)})/k(S + \text{olefin (1)})$. ^b Average yields, on the basis of $R^0(CO) - R(CO)$.

The measured values of relative rate constants are tabulated in Table III in comparison with the corresponding literature data for oxygen and selenium atom reactions.

Table III. Relative Rates of Addition of S(³P), O(³P), and Se(³P) Atoms to Olefins.

Olefin	O(³ P) ^a	Se(³ P) ^b	S(³ P)
Ethylene	1.00	1.00	1.00
Propylene	5.75	2.6	6.9
<i>trans</i> -Butene-2	28.3	56	20
<i>cis</i> -Butene-2	23.8	23.9	16
1-Butene	5.75	7.1	10
Isobutylene	25.0	44.7	50
Pentene-1	...	5.0	10
2-methyl-butene-1	56
Cyclopentene	29.8	...	18
Vinyl chloride	...	1.3	1.4

^a Reference 6. ^b Reference 11.

bf Relative Rates of Addition of S(¹D) Atoms. Relative rates of addition were determined for ethylene, propylene, and isobutylene. Product distributions and ratios, as measured by gc, are reported in Table IV. At least five experiments were performed at various conversions, and since secondary decompositions were negligible the table lists average values, reproducible to $\pm 10\%$.

Table IV. Addition of S(¹D) Atoms to Ethylene, Propylene, and Isobutylene. Product Distributions in Competitive Systems

Olefins	Rates, $\mu\text{mole}/\mu\text{mole of CO}$		Episulfide ratio (2)/(1)	Total product ratio
	Mercaptan	Episulfide		
(1) C ₂ H ₄ ^a	0.164 ^b	0.147 ^b	2.93	1.72
(2) C ₃ H ₆ ^a	0.103 ^b	0.431 ^b		
(1) C ₃ H ₆ ^c	0.094 ^d	0.161 ^d	2.55	2.02
(2) <i>i</i> -C ₄ H ₈ ^c	0.105 ^d	0.411 ^d		

^a $P(\text{COS}) = 91$, $P(\text{C}_2\text{H}_4) = P(\text{C}_3\text{H}_6) = 151$ torr. ^b Average of five experiments; CO = 3–4 μmoles . ^c $P(\text{COS}) = 77$, $P(\text{C}_3\text{H}_6) = P(i\text{-C}_4\text{H}_8) = 130$ torr. ^d Average of six experiments; CO = 3–6 μmoles .

The propylene–isobutylene rate constant ratio was also examined for a 1:1 mixture at a total olefin pressure of 3.06 torr; two mass spectrometric determinations gave $k(\text{S} + i\text{-C}_4\text{H}_8)/k(\text{S} + \text{C}_3\text{H}_6) = 2.01 \pm 0.08$, and therefore the rate constant ratio seems to be independent of total olefin pressure.

Discussion

The general kinetic features of the olefins examined here are very similar to those found earlier for the lower molecular weight compounds. The three principal products are episulfide and alkenyl- and vinylic-type mercaptans. The relative mercaptan yield is pressure dependent and exhibits a rising trend with increasing olefin pressures up to several hundred torr and a decreasing trend with added CO₂ pressure.

With cyclopentene (Figure 1) the alkenyl mercaptans, cyclopentene-3-thiol and cyclopentene-4-thiol, account for about 44% of the total product yield. The proportion of these mercaptans was 2:1, and they probably arise from statistical insertion at the 3 and 4 positions, respectively. Small yields of the vinylic mercaptan, cyclopentene-1-thiol, up to *ca.* 5% of the total, were also found, which is the first instance that a nonterminal

vinyl mercaptan from the reaction of $S(^1D)$ atoms with an olefin could be detected. The tautomeric equilibrium between the 1-thiol and thioketone proceeds spontaneously at room temperature, but it is strongly shifted (ca. 80%) to the thiol side.³

Product recoveries varied with experimental conditions, and the optimum values were 77% for the Hg arc and 60% for the Cd-lamp experiments. The loss was probably due to some polymerization process or cracking reactions. It has been shown elsewhere⁵

(5) A. R. Knight, O. P. Strausz, S. M. Malm, and H. E. Gunning, *J. Am. Chem. Soc.*, **86**, 4243 (1964).

that the photolysis of COS at 2288 Å produces translationally "hot" $S(^1D)$ atoms; under these conditions, the rate of insertion, relative to abstraction, increases, and collisional stabilization of the vibrationally excited products is less efficient. This explains the higher $R(M)/R(E)$ values and lower product yields in the shorter wavelength photolysis. In the reaction of $O(^3P)$ atoms with cyclopentene, one of the major products is ethylene (27%) formed in a pressure-independent fragmentation.⁶ The exothermicity resulting from the

(6) R. J. Cvetanovic, *J. Chem. Phys.*, **30**, 19 (1959).

addition of $S(^1D)$ and $O(^3P)$ atoms is nearly equal; but we found no direct evidence for a similar cracking with sulfur.

The effect of CO_2 on the reaction (Figure 2) is explained in terms of electronic relaxation of the excited $S(^1D)$ atoms to the ground state.



It has been shown^{1b,7} that mercaptans arise solely from

(7) A. R. Knight, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **85**, 1207, 2349 (1963).

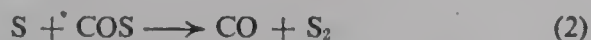
$S(^1D)$ atom precursors, whereas episulfides are formed from $S(^3P)$ and/or $S(^1D)$ atoms. If we take the relative yield of mercaptan as a measure of the $S(^1D)$ atom concentration in the system, at 1250 torr of added CO_2 more than 90% of the $S(^1D)$ atoms are quenched.

The CO yield is also slightly retarded by CO_2 . It is known from previous studies^{8,9} that the rate constant

(8) K. S. Sidhu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, *ibid.*, **88**, 2412 (1966).

(9) B. O'Callaghan, O. P. Strausz, and H. E. Gunning, to be published.

ratio $k(S + \text{olefin})/k(S + \text{COS})$ is at least 30 times larger for triplet than singlet S atoms. Consequently, conversion of $S(^1D)$ to $S(^3P)$ will diminish the significance of the abstraction step



with a concomitant decrease in $R(CO)$ to the limiting value, $R^0(CO)/2$. This should be accompanied by an increase in episulfide yields such that $R(\text{episulfide})/R(CO) = 1$, which, however, never obtains. This deficiency, in agreement with earlier observations,^{1b} suggests that the hot episulfides even from triplet atom addition undergo polymerization reactions with olefins very readily, and that the abstraction of sulfur by S atoms to form S_2 and olefin is fairly rapid.

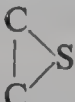
From the few experiments carried out with cyclohexene, it appears that this olefin behaves similarly to cyclopentene with the exception that, owing to the larger number of CH_2 groups in the molecule, the relative mercaptan yield is somewhat higher than in cyclopentene.

21

The behavior of cyclo-C₄F₆ is interesting in that it reveals a drastic decrease in π -bond reactivity caused by the strong electron-withdrawing power of fluorine atoms and thereby provides additional evidence for the electrophilic nature of sulfur atom attacks (*vide infra*) on olefinic π bonds. Furthermore, the stability of cyclo-C₄F₆ episulfide is low, and its probable mode of decay is the bimolecular reaction,



The reactions of sulfur atoms with mono- and dimethylsubstituted ethylenes have been reported earlier.^{1b,c} In order to complete the series we have examined the reaction with tri- and tetramethylethylene. The mercaptan yields in these reactions were 42 and 50% (in the pressure stabilization region), respectively. Thus with progressive methyl substitution in ethylene the yield of the methyl insertion product rises gradually from 20 to 50% of the total. Since the rate of S(¹D) insertion per C-H bond should not be greatly dependent on the number of methyl groups in the molecule, the relative reactivity of the π bonds in the series can be estimated. This turns out to be approximately constant. On the other hand, the relative rate measurements for ethylene, propylene, and isobutylene (Table IV) indicates a moderate increase in π -bond reactivity with increasing methyl substitution in the molecule. The apparent contradiction can be resolved by invoking a steric effect exerted by the methyl groups on the

incipient  S bond. The problem will be discussed further below.

The reaction with vinyl chloride leads to the formation of episulfide and smaller amounts of 1-chloroethene-2-thiol. It is seen from the pressure study (Figure 4) that the kinetics of this system again follows the established trend. Product recoveries were somewhat lower, up to 46%, than with other olefins.

The major reactions of S(¹D) atoms with 1,2-dichloroethenes leads to polymerization. Thermalized S(³P) atoms add stereospecifically to the double bond to yield predominantly *cis* or *trans* episulfides from *cis*- or *trans*-1,2-dichloroethene, respectively, proving the generality of the stereospecific nature of triplet S-atom additions.

The products obtained from the tetramethyl- and chloroethylene reactions have not been described previously in the literature; this is probably their first reported synthesis.

In the relative rate studies (Table III), triplet sulfur atoms were obtained by the collisional relaxation of excited singlet atoms. In a concurrent study⁹ triplet atoms were produced directly by the Hg(³P₁) photosensitization of COS, and rate constants were measured for ethylene, propylene, and isobutylene addition. The values obtained, 1:6.8:56, respectively, are in good agreement with the present determination.

A comparison of relative rates of sulfur atom addition to those reported by Cvetanović, *et al.*, for oxygen,¹⁰ and

(10) R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

Callear and Tyerman for selenium,¹¹ reveals an im-

(11) A. B. Callear and W. J. R. Tyerman, *Proc. Chem. Soc.*, 296 (1964); private communications.

pressive correlation between the chemical reactivity of the oxygen group elements. All three species exhibit a clear electrophilic tendency, first shown by Cvetanović for oxygen, in that the reactivity of the ground-state atoms increases with increasing electron-donating power of the olefin molecule.

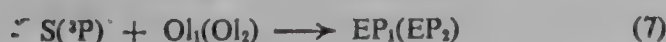
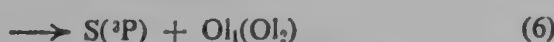
In spite of the broad agreement some dissimilarity is also apparent in the fine details. The entropy factor of the oxygen addition is invariant with olefin structure, and the variation in rates is due entirely to activation energy effects. For selenium, the entropy factor changes, but with no obvious trend, and for sulfur a definite trend appears. This is evident from the 2-butene data. Substitution of a methyl group in ethylene causes a sevenfold rate increase. A second methyl on the same carbon causes a further sevenfold increase, but on the neighboring carbon only a *ca.* threefold increase. This is in spite of the fact that the ionization potentials, localization, and excitation energies, which largely determine the magnitude of the activation energy of the process, are nearly identical for the three isomeric butenes. Similar trends have been observed for monovalent electrophilic radical additions and attributed to the steric hindrance of the methyl groups. A compilation of the relevant data is given in Table V, in all cases isobutylene is the most reactive and *trans*-2-butene is only slightly more reactive than the *cis* isomer.

Table V. Relative Rates of Addition of H Atoms, Br Atoms, and CH₃ and CF₃ Radicals to Olefins

Olefin	H ^a	Br ^b	CH ₃ ^c	CF ₃ ^d
C ₂ H ₄	1.0	1.0	1.0	1.0
C ₃ H ₆	1.5	18	1.3	1.2
1-C ₄ H ₈	...	23	1.6	...
<i>i</i> -C ₄ H ₈	4.5	384	2.1	3.7
<i>cis</i> -C ₄ H ₈	0.9	95	0.08	0.86
<i>trans</i> -C ₄ H ₈	1.1	99	0.15	1.0

^a K. Yang, *J. Am. Chem. Soc.*, 84, 3795 (1962). ^b I. Abell, *Trans. Faraday Soc.*, 60, 2214 (1964). ^c G. E. Owens, Jr., J. M. Pearson, and M. Szwarc, *ibid.*, 61, 1722 (1965). ^d A. P. Stefani, L. Herk, and M. Szwarc, *J. Am. Chem. Soc.*, 83, 4732 (1961).

The data on the relative rates of S(¹D) atom additions (Table IV) is valuable in spite of its limited range because of the scarcity of information on the relative reactivity of atoms in their different electronic levels. In the competitive systems involving S(¹D) atoms, the evaluation of rate constants is complicated by the possibility of singlet → triplet deactivation. The following reaction scheme is considered



where Ol₁ and Ol₂ are the two olefins and M₁, M₂ and EP₁, EP₂ are the respective mercaptans and episulfides.

If episulfides are formed only from the addition of triplet atoms, then the observed episulfide ratio should correspond to that obtained for $S(^3P)$ atom addition. The data in Tables III and IV show that this is not the case, and therefore the episulfide-forming step must involve the participation of $S(^1D)$ atoms.

It is also clear that $S(^1D)$ atoms are less selective than (^3P) atoms. Upper limits for the relative rate constants are 1, 2.9, and 7.5 for ethylene, propylene, and isobutylene, respectively. The relative importance of $S(^1D)$ addition cannot be evaluated from the present study. It is estimated that 70% or more of the episulfides are formed from singlet atoms. The data can best be rationalized by assuming that the same factors influence the rates of addition of both species; that is, the rate increases with increasing alkyl substitution in the olefin. A lowering in the activation energy and the consequent decrease in selectivity for the excited-atom reaction is not surprising, since the intersection of the corresponding potential energy surfaces in this case occurs at 26 kcal/mole higher energy and equivalently longer intermolecular separation. Assuming similar contours for the repulsive potentials, this results in lowering the energy separation of the point of intersection from that of the separated olefin + S-atom surface, which determines the magnitude of the activation energy barrier.

In intermolecular competing reactions, the π -bond reactivity increases in the order ethylene < propylene < isobutylene, whereas the intramolecular competition between mercaptan and episulfide formation suggests that the π -bond reactivity in the series propylene, 2-butene, trimethylethylene, and tetramethylethylene (*vide supra*) is the same. The discrepancy can be resolved if it is assumed that in the α,β -methylated ethylenes the methyl groups exert a steric hindrance, compensating for the increased reactivity of the π bond. Thus the interpretation of both $S(^3P)$ and $S(^1D)$ atom reactivity makes it necessary to invoke steric hindrances in methylated ethylenes.

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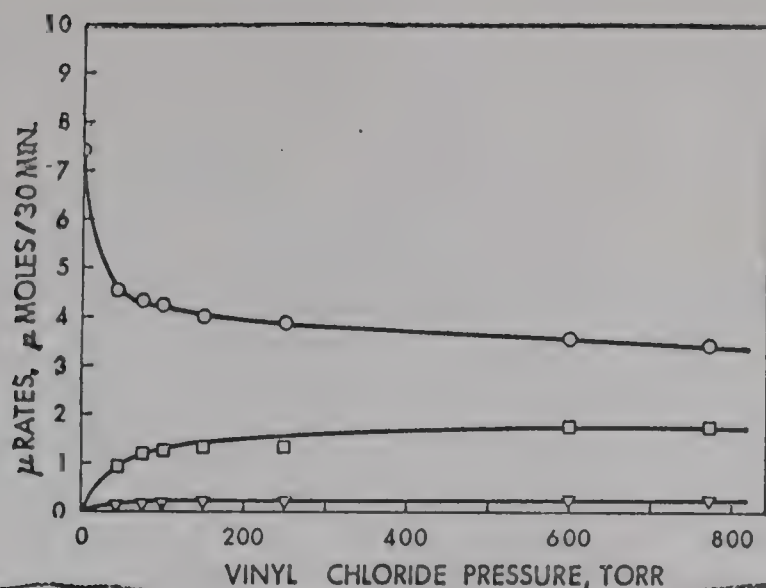


Figure 1. Addition of sulfur atoms to cyclopentene. Rates of product formation as a function of cyclopentene pressure: O, CO; ∇ , cyclopentene episulfide; \square , cyclopentene-3-thiol + cyclopentene-4-thiol; \bullet , cyclopentene-1-thiol.

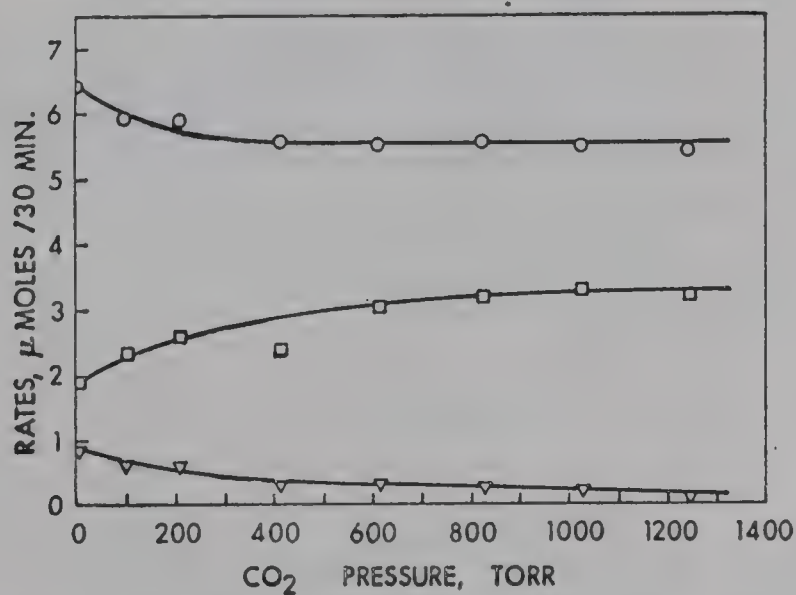


Figure 2. Addition of sulfur atoms to cyclopentene. Rates of product formation as a function of CO_2 pressure: O, CO; ∇ , cyclopentene-3-thiol + cyclopentene-4-thiol; \square , cyclopentene episulfide.

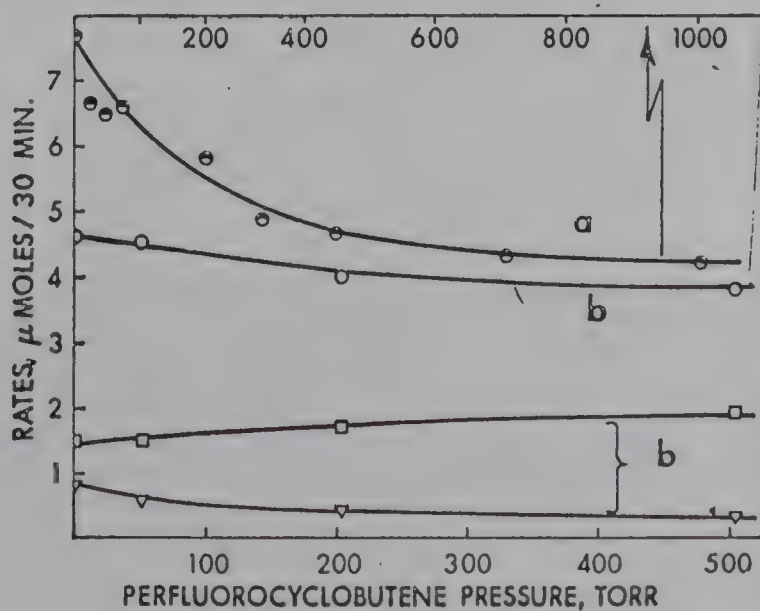


Figure 3. (a) Rates of product formation as a function of perfluorocyclobutene pressure ($P(\text{COS}) = 100$ torr): \bullet , CO (upper scale). (b) Addition of sulfur atoms to cyclopentene. Rates of product formation as a function of perfluorocyclobutene pressure (lower scale) ($P(\text{COS}) = 100$ torr, $P(\text{cyclo-C}_5\text{H}_{10}) = 75$ torr): O, CO; \square , cyclopentene episulfide; ∇ , cyclopentene-3-thiol + cyclopentene-4-thiol.

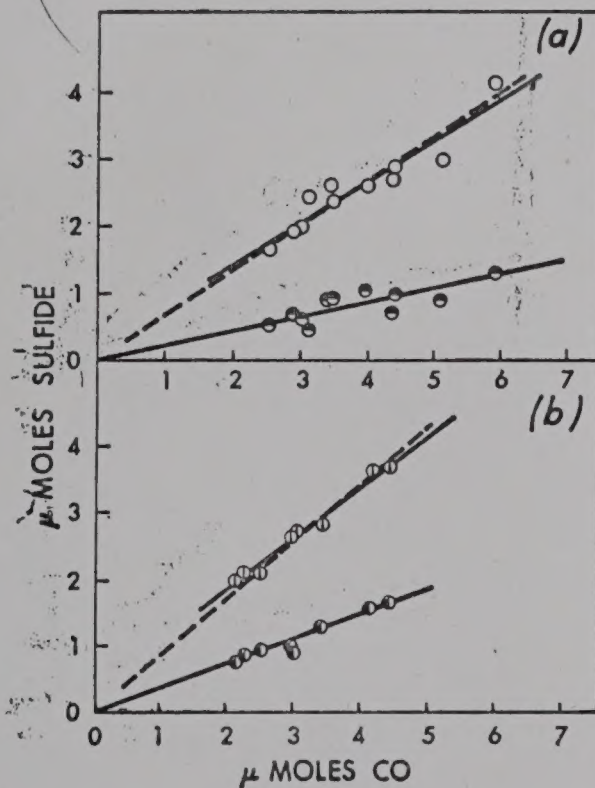
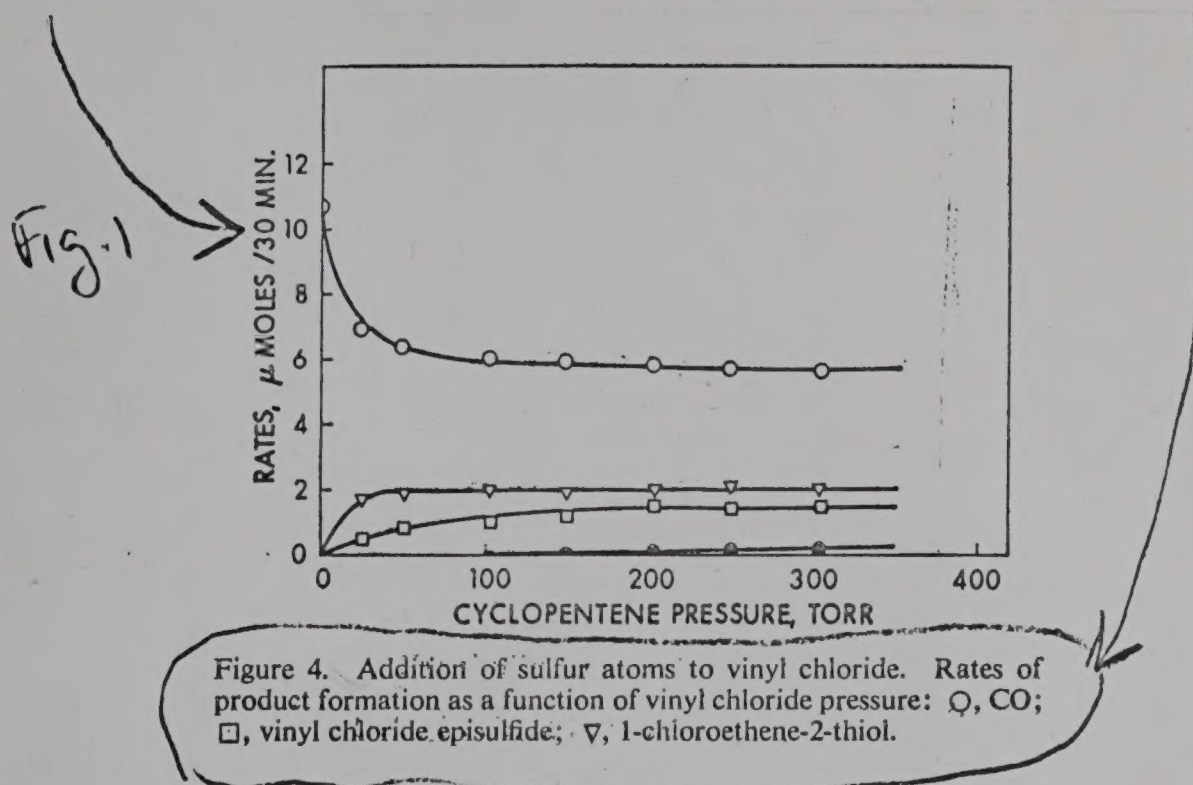


Figure 5. (a) Addition of $S(^3P)$ atoms to propylene and *trans*-2-butene. Sulfide vs. CO yields for $[C_3H_6]/[C_4H_8] = 1.42$ ($P(CO_2) = 1223$, $P(COS) = 31.5$, $P(C_3H_6) = 25.5$, $P(trans-2-C_4H_8) = 18.0$ torr): \bullet , propylene sulfide; \circ , *cis*- + *trans*-2-butene sulfide $\times 1.42$. (b) Addition of $S(^3P)$ atoms to propylene and *trans*-2-butene. Sulfide vs. CO yields for $[C_3H_6]/[C_4H_8] = 2.63$ ($P(CO_2) = 1244$, $P(COS) = 32.2$, $P(C_3H_6) = 44.7$, $P(trans-2-C_4H_8) = 17$ torr): \bullet , propylene sulfide; \circ , *cis*- + *trans*-2-butene sulfide $\times 2.63$.

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